

**ADSORPTIVE REMOVAL OF Cr(VI) AND Al(III) FROM  
AQUEOUS SOLUTION BY SUGARCANE BIOMASS**



**A Dissertation**

**Submitted as a partial fulfillment for the requirement of**

**Master's Degree of Science in Chemistry**

**By**

**Paramatma Mishra**

**Symbol No. : 5684**

**T. U. Regd. No. : 5-2-55-638-2001**



**Tribhuvan University**

**Institute of Science and Technology**

**Department of Chemistry**

**Tri-Chandra Multiple Campus**

**Ghantaghar, Kathmandu, Nepal**

**May, 2012**

**Tribhuvan University**  
**Institute of Science and Technology**  
**Tri-Chandra Multiple Campus, Department of Chemistry**  
**Ghantaghar, Kathmandu**  
**Nepal**

***LETTER OF APPROVAL***

The dissertation entitled

***“ADSORPTIVE REMOVAL OF Cr(VI) AND Al(III) FROM AQUEOUS SOLUTION BY  
SUGARCANE BIOMASS”***

**Submitted by**

**Paramatma Mishra**

Symbol No. 5684

T.U. Regd. No. : 5-2-55-638-2001

has been accepted as a partial fulfillment of the requirement for the

**Master's Degree in Chemistry.**

.....  
**Head**

Mrs. Bimaleswori Pradhan,  
Department of Chemistry,  
Tri-Chandra Multiple Campus,  
Ghantaghar, Kathmandu  
Nepal

.....  
**Co-ordinator**

Prof. Dr. Shiba Ram Vaidya  
M.Sc. Program  
Department of Chemistry,  
Tri-Chandra Multiple Campus,  
Ghantaghar, Kathmandu  
Nepal

.....  
**External**

Asso. Prof. Dr. Megh Raj Pokhrel  
Central Department of Chemistry,  
Tribhuvan University  
Kirtipur, Kathmandu  
Nepal

.....  
**Internal**

Mr. Surendra Gautam  
Department of Chemistry,  
Tri-Chandra Multiple Campus  
Ghantaghar, Kathmandu  
Nepal

.....  
**Supervisor**

Dr. Deba Bahadur Khadka  
Central Department of Chemistry,  
Tribhuvan University  
Kirtipur, Kathmandu  
Nepal

## FOREWORD

The entire dissertation task entitled “*ADSORPTIVE REMOVAL OF Cr(VI) AND Al(III) FROM AQUEOUS SOLUTION BY SUGARCANE BIOMASS* ” is submitted by Mr. Paramatma Mishra for the partial fulfillment of M.Sc. degree in chemistry of Tribhuvan University is carried out under my supervision. No part of this dissertation has been submitted for any other degree.

---

### Supervisor

Dr. Deba Bahadur Khadka  
Central Department of Chemistry  
Tribhuvan University  
Kirtipur, Kathmandu  
Nepal

**May, 2012**

## ACKNOWLEDGEMENT

I am grateful to express my profound thanks and heartfelt gratitude to my research supervisor Dr. Deba Bahadur Khadka, Central Department of Chemistry, Tribhuvan University for the help and guidance rendered to me at every stage of my work. Without his proper guidance and constructive remarks, this work wouldn't have been a reality.

I would also wish to thank Prof. Dr. Shiba Ram Vaidya, Co-ordinator of M.Sc. program of Tri-Chandra Multiple Campus for providing me this opportunity and kind co-operation during the entire work. I would also like to thank all the staffs of M.Sc. program of Tri-Chandra Campus for providing me essential remarks along with laboratory facility to conduct this work.

I am obliged to Assoc. Prof. Dr. Kedar Nath Ghimire, Head, Central Department of Chemistry, T.U., Kirtipur for his valuable suggestions for the work.

Lastly, I am very thankful to my family members and friends for believing me and supporting me unconditionally in whatever I do. Last but not the least I am grateful to my loving brother Shubhashish Mishra for his creative output computer typing and setting of matters.

Paramatma Mishra

**May, 2012**

## ABSTRACT

The potential and effectiveness of activated carbon derived from carbonization of sugarcane bagasse (*Saccharum officinarum*) for adsorptive removal of Cr(VI) and Al(III) was examined by adsorption technique. Activated carbon was prepared by subjecting the raw sugarcane bagasse to chemical modification using concentrated sulphuric acid in (1:2) (w/v) of ratio of adsorbent weight to volume of concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Boehm method was used to estimate the oxygen containing functional groups. The acidic functional groups, specific surface area and adsorptive capacity all greatly increased with chemical modification. The batch removal of Cr(VI) and Al(III) from aqueous solution was investigated. The influence of pH, initial concentration of metal ion and contact time were also investigated. The maximum adsorption capacity of Cr(VI) was found to be 131.68 mg/g at optimum pH of 1 and the maximum adsorption capacity of Al(III) was found to be 125.89 mg/g at optimum pH of 6 at the laboratory temperature respectively. The equilibrium time for Cr(VI) and Al(III) were found to be 180 and 120 minutes respectively. Kinetics of adsorption was found to follow pseudo-second order model. Both Langmuir and Freundlich adsorption isotherm could be used to describe adsorption isotherm but the Langmuir isotherm was found to be in good agreement with experimental data.

# Table of Contents

**Foreword**

**Acknowledgement**

**Abstract**

**Abbreviations**

<b>1. Introduction</b>	<b>1-9</b>
1.1 General Introduction	
1.2 Adsorption Study	
1.3 Chemical Modification of Adsorbent	
1.4 Characterization of Adsorbent	
1.4.1 Determination of Surface Area	
1.4.2 Scanning Electron Microscopy	
1.4.3 Infrared Spectra Analysis	
1.4.4 Functional Group Determination: Boehm Titration	
1.5 Determination of Chromium Cr(VI) and Aluminium Al(III)	
1.6 Adsorption Isotherms	
1.7 Adsorption Kinetics	
1.7.1 Pseudo-First Order Model	
1.7.2 Pseudo-Second Order Model	
1.7.3 Second Order Model	
<b>2. Literature Survey</b>	<b>10-12</b>
<b>3. Objective of the Present Study</b>	<b>13</b>
3.1 General Objectives	
3.2 Specific Objectives	
<b>4. Limitations of the Study</b>	<b>14</b>
<b>5. Experimental</b>	<b>15-20</b>
5.1 Preparation of Reagents	
5.1.1 Stock Solution of Cr(VI) and Al(III)	
5.1.2 Working Solution of Cr(VI) and Al(III)	
5.1.3 5N Sulphuric Acid (H <sub>2</sub> SO <sub>4</sub> ) Solution	
5.1.4 5N Nitric Acid (HNO <sub>3</sub> ) Solution	
5.1.5 5M Sodium Hydroxide (NaOH) Solution	
5.1.6 Preparation of 0.25% 1,5 Diphenyl Carbazide (DPCI) Solution	
5.1.7 Preparation of 0.2% Eriochrome Cynine R (ECR) Solution	
5.1.8 Preparation of Buffer Solution of pH 4.0, 7.0 and 9.2	
5.2 Preparation of Adsorbent from Sugarcane Bagasse	
5.2.1 Preparation of Adsorbent from Raw Sugarcane Bagasse	
5.2.2 Preparation of Charcoal from Raw Sugarcane Bagasse	

5.3	Determination of Metal Ion Solution	
5.3.1	Determination of Cr(VI)	
5.3.2	Determination of Al(III)	
5.4	Adsorption Study	
5.4.1	Batch Adsorption Study	
5.4.2	Batch pH Studies	
5.4.3	Effect of Metal Ion Concentration	
5.4.4	Batch Kinetics Studies	
5.5	Characterization of the Charcoal	
5.5.1	Surface Area Determination	
5.5.2	Scanning Electron Microscopy (SEM) Image of the Charcoal	
5.5.3	Infrared Spectra (I R) Analysis	
5.5.4	Titrimetric Method (Boehm Titration)	
<b>6.</b>	<b>Results and Discussion</b>	<b>21-25</b>
6.1	Absorption Spectra & Calibration Curve	
6.1.1	Calibration Curve for Cr(VI) with DPCI	
6.1.2	Calibration Curve for Al(III) with ECR	
6.2	Characterization of Charcoal	
6.2.1	Surface Area Determination	
6.2.2	Scanning Electron Microscopy (SEM) Image of the Charcoal	
6.2.3	Infrared Spectra (IR) Analysis	
6.2.4	Titrimetric Method (Boehm Titration)	
6.3	Batch Adsorption Studies	
6.3.1	Batch pH Studies	
6.3.2	Batch Isotherm Studies	
6.3.3	Batch Kinetics Studies	
	<b>Figures</b>	<b>26-36</b>
<b>7.</b>	<b>Conclusion</b>	<b>37</b>
	<b>References</b>	
	<b>Appendix</b>	

## Abbreviations

%	Percentage
A%	Adsorption percentage
mg/L	Milligram per liter
g/L	Gram Per liter
µg/L	Microgram per liter
nm	Nanometer
µm	Micrometer
M	Molarity
N	Normality
ppm	Parts per million
mg/g	Milligram per gram
mL	Milliliter
meq/g	Milliequivalent per gram
cm	Centimeter
cm <sup>2</sup> /mol	Centimeter square per mole
mol/L	Mole per liter
g/mg.min	Gram per milligram per minute
conc.	Concentrated
min	Minute
hr	Hour
DPCI	1,5-Diphenylcarbazide
ECR	Eriochrome Cyanine R
RSCB	Raw Sugarcane Bagasse
MSCB	Modified Sugarcane Bagasse
BET	Brunauer-Emmett-Teller
i.e.	That is
et al.	And others
$c_i$	Initial concentration of metal ion in mg/L
$c_e$	Equilibrium concentration of metal ion in mg/L
$c_t$	Concentration of metal ion in mg/L at time “t”
$q_m$	Maximum adsorption capacity in mg/g
$q_e$	Amount of metal ion adsorbed per gram at equilibrium
$q_t$	Amount of metal ion adsorbed per gram at time “t”
b	Adsorption constant in L/mg
k	Adsorption capacity
1/n	Adsorption intensity
R <sup>2</sup>	Regression coefficient
$k_1$	Pseudo-first order rate constant
$k_2$	Pseudo-second order rate constant
h	Initial adsorption rate
$k_L$	Langmuir parameter
$\lambda_{max}$	Maximum wavelength



SEM	Scanning Electron Microscopy
IR	Infrared spectroscopy
LR	Laboratory reagent
S N	Serial number
Opt.	Optimized
pH	Potential of hydrogen
pH <sub>i</sub>	Initial pH
pH <sub>e</sub>	Equilibrium pH
A	Absorbance or optical density
L	Path length of absorbing medium in cm
R <sub>L</sub>	Dimensionless constant separation factor
[J]	Concentration of absorbing species in moles/liter (mol/L)
I <sub>o</sub>	Intensity of the incident radiation
I	Intensity of the transmitted radiation
ε	Molar extinction coefficient
NAST	Nepal Academy of Science and Technology

# 1 Introduction

## 1.1 General Introduction

Environmental pollution due to the development in technology is one of the most important problems of this century. Heavy metals like chromium (Cr), lead (Pb), mercury (Hg), arsenic (As), cadmium (Cd), copper (Cu), aluminium (Al), nickel (Ni) in waste water are hazardous to the environment. These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living materials. Besides, heavy metals discharge in the wastewater can be toxic to aquatic life and render natural waters unsuitable for human consumption.<sup>1</sup> Both Cr(VI) and Al(III) are toxic to animals and plants. The tolerable limit of Cr(VI) for drinking water is 0.05 mg/L.<sup>2</sup> and that of Al(III) for drinking water is 0.2 mg/L.<sup>3</sup>

Chromium is priority metal pollutant introduced into water bodies from many industrial processes such as tanning, metal processing, paint manufacturing, steel fabrication and agricultural run off. Chromium is also used in explosive ceramic and photography. Chromium occurs in the aquatic environment as both trivalent and hexavalent states. Hexavalent chromium, which is primarily present in the form of chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) ions possess significantly higher levels of toxicity than the other valency states.<sup>4</sup> The toxicity of Cr(VI) is well documented and it is considered a hazard to health of man and animals. The various compounds of chromium are found to be both corrosive to flesh and carcinogenic. The presence of Cr(VI) in the aquatic environment at high concentration is lethal to marine species.<sup>5</sup>

Al is the most abundant metal in the earth's crust with a mean concentration in the earth's upper crust of 8.1%. In most natural water the concentration of Al is low due to its limited solubility. Its solubility increases at lower pH and by complexation with fluoride or organic substances. Al has now known essential biological role for animals or plants. For many years it was thought to be virtually non toxic. Recent experiments have shown otherwise. It is now well documented that dialysis fluids containing Al are the cause of a potentially lethal condition called dialysis encephalopathy. The condition is caused by a slow degeneration of brain tissue brought about by Al introduced into the bloodstream via the dialysis unit. Al ingested with food is normally taken upto small extent only is rapidly excreted as long as the kidneys working properly. Plants and trees also suffer from high levels of Al in the root zone. Aquatic invertebrates seem generally not to be as sensitive to Al as fish, although some toxic effects have been shown.<sup>6</sup>

In aqueous solution Al exists in a no. of complexes, all in dynamic equilibrium. The free aqua-ion  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ , is acidic, and hydrolysis even below pH 3. With increasing pH monomeric hydroxo complexes are formed. If the pH is increased still further, polymerization can occur. The exact nature of these polymers complexes are still under debate. The main inorganic ligands apart from hydroxide, is fluoride, that forms very strong complexes with Al. In natural water sulfato, carbonato, phosphato

and silicato complexes also exist. Most organic compounds containing combinations of carboxylic and hydroxyl groups form complexes with Al.<sup>6</sup>

The commonly used procedures for removing metal ions from effluents include chemical precipitating, lime coagulation, ion exchange, reverse osmosis and solvent extraction adsorption. These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products. Most of these methods are often ineffective or uneconomical when heavy metal concentration is higher (10-100 mg/L) than permissible concentration (<1 mg/L). An efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content.<sup>7</sup>

Among all the methods, adsorption is highly effective and economical. Moreover adsorption processes for waste water treatment have had a long history and also it is a method that necessitates careful design but with little maintenance. A number of adsorbents such as zeolites, clay, biosorbents, manganese dioxide, ground nut husk, red mud, bone charcoal, juniper park, sugarcane bagasse, rice husk, perlite and activated charcoal have been used in the adsorptive removal of heavy metal ions from water system.<sup>8</sup>

Among all these adsorbents, activated carbon has been widely used in water treatment to remove organic and inorganic pollutants due to its high adsorption capacity. The capacity of carbon is related to its physical and chemical properties such as porosity, specific surface area, surface functional groups and surface additives in connection with preparation conditions. In spite of its effectiveness in the removal of heavy metals from waste waters, the high cost of commercial activated carbon has restricted its wide spread use. A lot of attentions had been directed towards the production of low cost activated carbon adsorbent derived from the cheaper and readily available carbonaceous material. Various agricultural waste materials like rice husk, coconut shell, peanut shell, rubber wood, fruit seeds, sugarcane bagasse, sawdust etc. are used to make activated carbon owing to the low cost of such carbon precursors.<sup>9</sup>

## 1.2 Adsorption Study

Adsorption is the concentration of substances on the surface of a solid or liquid. The adsorption of various metals onto adsorbent can be studied by column and batch experiments.

In column adsorption method, a column of adsorbent of particular length and internal diameter is made and effluent is allowed to flow through a reservoir at the top using a flow controller. The treated water is collected at the bottom through orifice. Samples of the outlet bulk solution are collected at definite intervals of time and examined for the residual metal content to evaluate the efficiency of the column.

In batch adsorption method, a predetermined mass of adsorbent is taken into the stoppered bottle with predetermined volume and concentration of the metal ions. The bottles were shaken at room temperature for about 24 hours to ensure adsorption equilibrium, after equilibrium the mixture is filtered and concentration is measured again by spectrophotometer. Metal adsorption onto different adsorbent is affected by using different parameters such as initial metal ion concentration, contact time, amount of adsorbent used, temperature and pH of the solution. Keeping one parameter changing and other constant the effect of each parameter can be studied.<sup>10</sup>

The amount of metal ion adsorbed in mg/g at equilibrium is computed by the following relationship:

$$q = \frac{(C_i - C_e)}{w} \times v \dots\dots\dots(i)$$

where  $c_i$  and  $c_e$  are the metal ion concentration in mg/L initially and at equilibrium respectively.  $v$  is the volume of the metal solution in liter and  $w$  is the weight of the adsorbent in grams.<sup>10</sup>

Metal removal percentage is defined as the ratio of the decrease in metal ion concentration before and after adsorption to the initial metal ion concentration. The percentage adsorption of metal ion (A%) is calculated by following relationship:

$$A(\%) = \frac{(C_i - C_e)}{C_i} \times 100 \% \dots\dots\dots(ii)$$

## 1.3 Chemical Modification of Adsorbent

Agricultural wastes are the biomass material having effective adsorption capacities. The adsorption efficiency of such agricultural waste can be enhanced by various methods such as activation, steam activation, chemical modification, and so on. The biomass material like sugarcane bagasse consists of cellulose (50%), hemicellulose (27%) and lignin (23%). The presence of these three biological polymers causes sugarcane bagasse rich in hydroxyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties. Chemical modification in generally improved the adsorption capacity of

adsorbents probably due to higher number of active binding sites after modification, better ion exchange properties and formation of new functional groups that favours metal uptake.<sup>11</sup>

Bagasse was collected from sugar mill located at Panga, Kirtipur. The collected bagasse was cleaned with distilled water, dried and grinded in mechanical grinder at Central Department of Chemistry, Kirtipur and sieved it to pass through 225 µm mess size. So obtained raw bagasse has lesser efficiency for Cr(VI) and Al (III) metal uptake. In order to enhance metal uptake capacities of raw bagasse it was subjected to chemical modification with concentrated sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) at ordinary temperature. The raw bagasse was mixed in (1:2) (w/v) adsorbent ratio with conc. H<sub>2</sub>SO<sub>4</sub> and allowed to leave for 24 hours at room temperature to ensure the complete reaction. Such chemical modification produces suitable surface matrix with high degree of micro porosity. The excess acid remained during chemical modification was removed by washing it with distilled water until pH of the modified bagasse reached to almost neutral. By chemical modification, effective surface area of carbon increases and surface of the adsorbent get modified due to the increase in concentration and or formation of different functional groups present in the adsorbent surface.<sup>12</sup>

## **1.4 Characterization of Adsorbent**

### **1.4.1 Determiration of Surface Area**

The extent of adsorption chiefly depends on surface area of the adsorbent. Greater is the surface area of the adsorbent, higher will be the adsorption of adsorbate. Surface area of the adsorbent can be determined by BET single point method passing nitrogen gas or by chemical/ dye adsorption. Surface area can be determined by using following relationship: <sup>13</sup>

$$S = (1/b) \times N \times 21 \times 10^{-20} \text{ m}^2/\text{g} \dots\dots\dots(\text{iii})$$

Where,

N stands for Avogadro's number

S stands for specific surface area

b stands for Langmuir constant

### **1.4.2 Scanning Electron Microscopy (SEM)**

The adsorbent made in this study were characterized by scanning electron microscopy (SEM). SEM image shows pore volume and nature of the surface of the adsorbents. Characterization by SEM image indicates that adsorbents bearing irregular, micro porous surface structure, high degree surface area with high chemical and mechanical stability is considered to have high surface area with efficient sorption capacity.<sup>14</sup>

### 1.4.3 Infrared Spectroscopy (IR)

Infrared spectroscopy (IR) is an important tool that deals with the interaction of infrared light with matter. The IR spectrum of a molecule is a graphical display. It shows the frequency of IR radiation absorbed and the percentage (%) of the incident light that passes through the molecule without being absorbed. Different functional groups present in the adsorbent can be identified by the analysis of IR spectra.<sup>14</sup>

### 1.4.4 Titration Studies (Boehm Titration)

According to H.P Boehm, only strong acidic carboxylic acid groups are neutralized by sodium bicarbonates, where as these neutralized by sodium carbonate are thought to be lactones, phenols and carboxyl groups. The weak acidic phenolic groups only react with strong alkali sodium hydroxide. Therefore, by selective neutralization using bases of different strength, the surface acidic functional groups in carbon can be characterized both quantitatively and qualitatively.<sup>15</sup>

### 1.5 Determination of Cr(VI) and Al(III)

For the determination of concentration of Cr(VI) and Al(III) ions, spectrophotometric method is employed. The theoretical basis of spectrophotometer is provided by Lambert-Beer law. This method is suitable for the determination of metal ion concentration. Interferences if present should be separated. However careful treatment of samples and correction for interferences are needed for the analysis of samples with low metal ion concentrations.

**Calibration Curve based on Lambert-Beer Law:** Calibration curve is the graphical plot of absorbance versus known concentration of metal ion. Calibration curve is based on the Lambert-Beer law. The calibration curve is determined by using spectrophotometer. Spectrophotometer is based on the absorption of light by particular wavelength by a particular color (in visible range). The absorption of light is related to concentration as given by Lambert-Beer law: <sup>16</sup>

$$A = \epsilon [J] L \dots\dots\dots(iv)$$

Where, A =  $\log I_0/I$  = absorbance

Where,  $I_0$  is intensity of incident light and

I is intensity of transmitted light

[J] is molar concentration of the sample (mol/L)

$\epsilon$  is molar extinction coefficient (L/mol.cm) or (cm<sup>2</sup>/mol) &

L is path length of the cell (cm)

For a particular type of spectrophotometer  $\mathcal{E}$  and  $L$  can be made constant.  
 Therefore,  $A \propto [J]$  or the value of absorbance can be related with concentration.

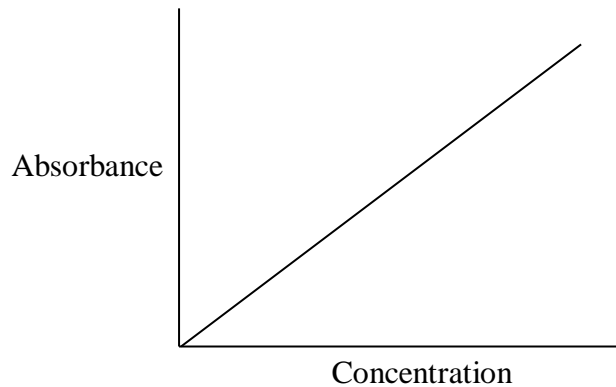


Figure i: Plot of Absorbance against Concentration

## 1.6 Adsorption Isotherm

Adsorption isotherm is a curve which relates the amount of adsorbate adsorbed per unit mass of adsorbent to the amount of unadsorbed adsorbate remaining in solution at equilibrium time. Several models have been developed to describe adsorption system behaviors. Langmuir and Freundlich adsorption isotherm are the most important isotherm and are generally used to analyze the adsorptive behavior of adsorbate on adsorbent.<sup>17</sup>

### 1.6.1 Langmuir Adsorption Isotherm

The Langmuir isotherm is the best known of all isotherms describing the adsorption of solute from the solution. This adsorption isotherm presumes homogeneous surface adsorption with the formation of monolayer on the adsorbent surface. The non-linear form of Langmuir (1916) equation can be written as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots\dots\dots(v)$$

where,  $q_e$  is the amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm)

$q_m$  is the amount of adsorbate adsorbed (mg) per unit mass of the adsorbent (gm) on complete monolayer formation, which is constant at fixed temperature.  $q_m$  is monolayer adsorption capacity and is determined solely by the nature of adsorbent.

$b$  is the adsorption constant (L/mg) related to the energy of adsorption or net enthalpy of adsorption.  $b$  is the value reciprocal of the concentration at which half the

saturation of the adsorbent is attained. Thus higher the value of  $b$  indicates the system attains equilibrium quickly.

$c_e$  is the equilibrium concentration of adsorbate (mg/L)

Equation (v) can be linearized as follow-

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{c_e}{q_m} \dots\dots\dots(vi)$$

From the experimental values of  $c_e$  and  $q_e$ , a plot of  $c_e/q_e$  against  $c_e$  can be drawn from which Langmuir parameters  $q_m$  and  $b$  can be evaluated. The plot gives a straight line with slope equal to  $1/q_m$  and intercept equal to  $1/q_m b$ . The values so obtained provide the information of quality of adsorbent. The adsorbent with the high value of  $q_m$  is preferred since it's adsorption capacity is high.<sup>18</sup>

The essential characteristics of Langmuir isotherm can be explained in terms of a dimensionless constant separation factor ( $R_L$ ) defined by,

$$R_L = \frac{1}{1 + K_L c_i} \dots\dots\dots(vii)$$

Where  $c_i$  is the initial concentration of the adsorbate (mg/L).  $K_L$  is the Langmuir equilibrium constant which is related with the affinity of binding sites. The value of  $R_L$  indicate the type of Langmuir isotherm to be irreversible ( $R_L=0$ ), favourable ( $0 < R_L < 1$ ) and linear ( $R_L=1$ ) or unfavourable ( $R_L > 1$ ).<sup>19</sup>

### 1.6.2 Freundlich Adsorption Isotherm

The variation of extent of adsorption with concentration can also be analyzed by the empirical equation given by Freundlich (1906). The non-linear form of Freundlich equation can be written as:

$$q_e = K c_e^{1/n} \dots\dots\dots(viii)$$

This model is based adsorption on heterogenous surface. The above equation (viii) can be written in logarithmic form as:

$$\log q_e = \log K + 1/n \log c_e \dots\dots\dots(ix)$$

where,  $q_e$  is the amount of metal ion adsorbed per gram of adsorbent at equilibrium (mg/g)

$c_e$  is equilibrium concentration of the adsorbent (mg/L)

$K$  is Freundlich constant indicating adsorption capacity (mg/g)

$1/n$  is characteristics constant for adsorption system (mg/L) i.e. it shows intensity of adsorption. The value of  $1/n$  lies between 0 and 1 indicates the favourable adsorption of metal ions.



The plot of  $\log q_e$  versus  $\log c_e$  should give a straight line with slope equal to  $1/n$  and the intercept on the y-axis equal to  $\log K$ .

This isotherm doesn't predict any saturation of the sorbent by the sorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface.<sup>18</sup>

## 1.7 Adsorption Kinetics

The study of rate and mechanism of adsorption phenomena is called the adsorption kinetics. It is one of the important characteristics in defining the efficiency of adsorbent. In order to understand adsorption kinetics of heavy metal ions, the adsorption process is studied monitoring percentage removal of heavy metals by the adsorbent at specified period of contact time.

The adsorption kinetics of heavy metal ions are generally described by the pseudo first order, pseudo second order and the second order rate equation. The experimental data obtained for adsorption at different interval of time is analyzed using pseudo first order and pseudo second order and second order kinetics.<sup>20</sup>

### 1.7.1 The Pseudo First-Order Model

The adsorption of metal ion on solid may be considered as a reversible reaction with equilibrium between two phases. Such process can be described by the pseudo first-order kinetics, according to Lagergren (1898) the pseudo first-order equation is generally expressed as,

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots\dots\dots(x)$$

Where,  $k_1$  (L/ min) is the rate constant of the pseudo first-order adsorption

$q_t$  (mg/g) is the amount of metal ion adsorbed at time  $t$  (min)

$q_e$  (mg/g) is the amount of metal ion adsorbed at equilibrium.

After integration and applying boundary condition  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , the integrated form of equation (x) is

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \dots\dots\dots(xi)$$

The plot of  $\log(q_e - q_t)$  versus  $t$  should give a straight line from which  $k_1$  and  $q_e$  can be determined from the slope and intercept of the plot respectively.<sup>21</sup>

### 1.7.2 The Pseudo Second Order Model

The pseudo second order kinetics rate equation is expressed as (Ho et al., 2000):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots\dots\dots(xii)$$

Where  $k_2$  is the rate constant of pseudo second order kinetics (g/mg.min)

After integration and applying boundary conditions  $q_t=0$  at  $t=0$  and  $q_t=q_t$  at  $t=t$  the above equation (xii) becomes,

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \dots\dots\dots(xiii)$$

On rearranging equation (xiii) we get,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

or,  $\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \dots\dots\dots(xiv)$

where,  $h = k_2 q_e^2 \dots\dots\dots(xv)$

the unit of 'h' is g/mg.min

The plot of  $t/q_t$  versus  $t$  of equation (xiv) should give a straight line from which  $q_e$  and  $k_2$  can be determined from the slope and intercept of plot respectively.<sup>22</sup>

### 1.7.3 The Second Order Model

The second order adsorption kinetic rate equation (Lagergren, 1898) is generally expressed as:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_{1/2} t \dots\dots\dots(xvi)$$

Where,  $q_e$  is amount of metal ions adsorbed at equilibrium (mg/g),  $q_t$  is the amount of metal ions adsorbed at time 't' (mg/g),  $t$  is contact time (min) and  $k_{1/2}$  is second order rate constant (g/mg.min). The plot of  $\frac{1}{q_e - q_t}$  versus  $t$  gives a linear plot, from which  $k_{1/2}$  and  $q_e$  can be determined from slope and intercept respectively.<sup>21</sup>

## 2. Literature Survey

The presence of certain heavy metals in aquatic system due to the natural as well as another progenic industrial activity is one of the most important sources of contamination which is quite responsible for several damages to the environment and adversely affecting health of the people as well as other living system. Removal of such heavy metals from aqueous solution is done by ion exchange, precipitation, electrolytic recovery, chelation solvent extraction and liquid membrane separation. Recently use of biological waste materials for heavy metals removal has been increasing because of being environmental friendly, cost effective and high metal uptake capacity.

Halya *et al.* (2000) studied the biosorption of Cr(VI) from aqueous solution on husk of bengal gram. The biosorptive capacity of the Bengal gram husk was dependent on the pH of the chromium solution, with pH 2 being optimal. The adsorption data fitted well with Langmuir and Freundlich isotherm models.<sup>23</sup>

Hamadi *et al.* (2001) studied the adsorption kinetics for the removal of Cr(VI) from aqueous solution by using tyre and saw dust. They found that the removal was favourable at low pH, with maximum removal at pH 2. They found both adsorbents were effective to remove Cr(VI) from solution. The sorption kinetics was found to follow pseudo-second order model.<sup>24</sup>

Say and Denizil (2001) studied the preparation of magnetic dye as adsorbent and its use in the removal of Al(III) ions. The maximum Al(III) adsorption was 722  $\mu\text{mol/g}$  polymer at pH 5. Non specific Al(III) adsorption was about 23  $\mu\text{mol/g}$  polymer under the same condition. Their aim was to prepare magnetic poly (2-hydroxyethylmethacrylate) (mPHEMA) adsorbent and to investigate the usability for the removal of Al(III) from drinking water and dialysis water. The adsorption behaviour was found to depend on pH, contact time and adsorbent dose.<sup>25</sup>

Gupta *et al.* (2003) studied the removal of cadmium and nickel from waste water using bagasse fly ash. They found maximum adsorption of cadmium and nickel occurred at concentration of 14 and 12 mg/L and at pH of 6 and 6.5 respectively with a sufficient adsorbent dose of 10 g/L. The adsorption data followed Langmuir model better than Freundlich model.<sup>26</sup>

Basyal and Ozdin (2004) studied the biosorption of Cr(VI) and Al(III) on *Chryseomonas Luteola* TEM05. They found the greatest capacity for Al(III) 55.2 mg/g and for Cr(VI) 3.0 mg/g at pH 5 and pH 4 respectively. The biosorption equilibrium was described by Langmuir and Freundlich isotherm. Freundlich isotherm fitted well for both ions. The kinetic data followed pseudo-second order model.<sup>27</sup>

Khan *et al.* (2004) studied the adsorption of cadmium on sugarcane bagasse from aqueous solution. The efficiency of adsorption was found to depend on the initial metal ion concentration, pH and contact time. Sugarcane bagasse an agricultural residue from sugar refining industries had been shown to have a great potential as a low cost adsorbent for Cd(II) removal and could be applied for waste water management strategies. Both Langmuir and Freundlich adsorption isotherms describe the sorption behaviour. The adsorption data followed pseudo-second order kinetics.<sup>28</sup>

Garg and Sud (2005) studied the adsorption behaviour of Cr(VI) onto modified sugarcane bagasse. They found there was almost complete adsorption (98%) of Cr(VI) with sugarcane bagasse treated with Citric acid at pH 2.0, stirring speed 50 rpm and adsorbent dose 2000 mg. The kinetic data shows that adsorption process follows Langmuir and Freundlich adsorption isotherm.<sup>9</sup>

Hatim and Fazara (2006) studied the effect of acidic treatment on metal adsorption of sugarcane bagasse activated carbon. They found that the chemically treated sugarcane bagasse remove 39.06 mg/g of Cu(II) at pH 5.0 which was 50% higher than the untreated sugarcane bagasse. They found that both Langmuir and Freundlich isotherm could be used to fit the data and estimate model parameter.<sup>11</sup>

Sankaramakishan and Sanghi (2006) prepared the novel xanthated chitosan with CS<sub>2</sub> in alkaline media and used to remove Cr(VI) from waste water. They found the maximum uptake of Cr(VI) to be 71 mg/g which was significantly more than plain chitosan 49 mg/g. The adsorption behaviour was pH dependent.<sup>29</sup>

Khan and Mohamad (2007) studied the adsorption of Cr(VI) on sugarcane bagasse. Chromium removal efficiency was found to be 70.2% at initial concentration of 10 mg/L at pH 1.0 and 4 hour contact time. The adsorption data for chromium fitted well to the Freundlich isotherm.<sup>30</sup>

Ghimire *et al.* (2007, 2008) studied the adsorption of metal ions onto cross linked seaweed, *Laminaria Japonica*. The maximum adsorption capacity for Cd(II), Pb(II) and Fe(II) was found to be 123, 380 and 85.45 mg/g respectively and was pH dependent. The experimental data was well fitted according to Langmuir adsorption isotherm. Ghimire *et al.*, also examined the adsorptive behaviour of phosphorylated orange waste loaded with Fe(III) for arsenic removal. The loading capacity for Fe(III) on phosphorylated orange gel was 67.57 mg/g higher than the gel prepared from cellulose 53.61 mg/g and found that arsenic removal efficiency was higher on the phosphorylated orange gel due to higher uptake capacity of gel on Fe(III). The uptake of Fe(II) was pH dependent and Langmuir adsorption model showed good agreement with the experimental data.<sup>31, 32</sup>

Bhattarai (2009) studied the adsorptive behaviour of chromium on raw rice husk and modified rice husk. The adsorptive behaviour was pH dependent. He found the maximum adsorptive capacity of modified rice husk for Cr(VI) was 190 mg/g at pH 1 which was much higher in comparison to raw rice husk. The adsorption data was best described by Langmuir isotherm and pseudo-second order kinetics.<sup>33</sup>

Raymundo *et al.* (2010) studied a methodology involving sugarcane bagasse bioadsorbent to remove the carcinogenic congo red dye from the aqueous solution. The result showed high efficiency with retention of 64% in synthetic congo red solution and 94% in effluent enriched with congo red at 10 g of adsorbent. The adsorption system provides a maximum adsorption capacity of 4.43 mg/g at pH 10. The equilibrium data fitted well with Langmuir adsorption isotherm.<sup>34</sup>

Humagai *et al.* (2010) studied the removal of cadmium, lead, nickel, zinc and copper from aqueous media by using charred xanthated sugarcane bagasse which was found to have significant adsorption capacity. The adsorption behaviour was pH dependent and the velocity of the sorption of the tested metal was fast reaching equilibrium within 40 minutes. The maximum loading capacity was found to be 225 for Cd(II), 318 for Pb(II), 144 for Ni(II), 164 for Zn(II) and 178 for Cu(II) mg/g respectively.<sup>35</sup>

Lara *et al.* (2010) studied the removal of lead from aqueous solution using sugarcane bagasse, agricultural waste. They modified the raw bagasse by sulphuric acid. The sorption capacity for lead of untreated bagasse and treated bagasse were 6.367 and 72.97 mg/g respectively at moderate temperature. The equilibrium sorption data were best described by Langmuir adsorption isotherm than Freundlich isotherm.<sup>36</sup>

Halim *et al.* (2011) studied the adsorption of Al(III) onto *Curcuma longa* (turmeric). The optimal removal of 95.8% was achieved at the 90<sup>th</sup> min. A dose of 6 g/L was enough for the 93% removal of Al(III) ion. Both Langmuir and Freundlich adsorption isotherm describes the sorption behaviour. The adsorption data follows pseudo-second order kinetics and the adsorption behaviour was pH dependent.<sup>37</sup>

### **3. Objectives of the Present Study**

Although, there are several conventional methods for removing Cr(VI) and Al(III) from aqueous solution, adsorption is one of the cost effective technique, which has been applied extensively in the waste water treatment process. A comparison has been made with raw and modified sugarcane bagasse adsorbent.

#### **3.1 General Objectives**

The general objective of the present work is to prepare low cost adsorbent from agricultural waste sugarcane bagasse and to investigate the adsorption capacity of the adsorbent for the sorption of Cr(VI) and Al(III) from aqueous solution.

#### **3.2 Specific Objectives**

The specific objectives of the present work are as follows:

- (i) To prepare, modify and characterize the adsorbent for the adsorption of Cr(VI) and Al(III) from synthetic aqueous solution.
- (ii) To investigate the effect of pH, initial concentration of adsorbate and contact time on the removal of Cr(VI) and Al(III) from aqueous solution.
- (iii) To investigate the equilibrium time of the acid modified sugarcane bagasse and raw sugarcane bagasse as an adsorbent for the removal of Cr(VI) and Al(III) from the aqueous solution.
- (iv) To study the kinetics of the sorption reaction and to find out the nature of adsorption isotherm in the removal of Cr(VI) and Al(III) from aqueous solution.
- (v) To compare the adsorption capacity of acid modified sugarcane bagasse carbon with raw sugarcane bagasse as an adsorbent.

#### **4. Limitations of the study**

- (i) Adsorption process was studied only with aqueous solution prepared in the laboratory.
- (ii) Characterization was done by determining surface area, SEM image and IR spectra analysis and Boehm titration.
- (iii) Due to unavailability of certified standard metal samples, chemicals available in the laboratory were directly used.
- (iv) Parameters like effect of temperature and adsorbent dose were not considered.

## **5. Experimental**

### **5.1 Preparation of the Reagent**

#### **5.1.1 Stock Potassium Dichromate ( $K_2Cr_2O_7$ ) Solution**

Stock potassium dichromate solution was prepared by dissolving 2.514 gm of potassium dichromate crystal in a 1000 ml volumetric flask in 0.1N nitric acid solution.

1ml of stock potassium dichromate solution= 1000  $\mu$ g of Cr(VI)

From this stock potassium dichromate solution, working solution of lower concentration was prepared by dilution method in 0.1 N nitric acid solutions.

#### **5.1.2 Working Solution of Potassium Dichromate in the form of Cr(VI)**

25 ml of the stock potassium dichromate solution was diluted to 250 ml volumetric flask in 0.1 N nitric acid solution.

1 ml of working chromium solution = 100  $\mu$ g/ml of Cr(VI)

By following similar dilution method, solution of 10 mg/L , 20 mg/L , 50 mg/L, 75 mg/L, 100 mg/L, 150 mg/L, 175 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, and 400 mg/L and so on were prepared in 0.1 N nitric acid solution.

#### **5.1.3 Aluminium Stock Solution [ $KAl(SO_4)_2 \cdot 12H_2O$ ]**

Stock aluminium solution was prepared by dissolving 17.584 gm of potash alum in 1000 ml volumetric flask in 0.1 N nitric acid solution.

1ml of the stock aluminium solution = 1000  $\mu$ g Al(III)

From this stock aluminium solution, working solution of lower concentration were prepared by dilution method in 0.1 N nitric acid solution.

#### **5.1.4 Working Aluminium Solution of Al(III)**

25 ml of the stock aluminium solution was diluted to 250 ml volumetric flask in 0.1 N nitric acid solution.

1 ml of working Al(III) solution = 100  $\mu$ g/ml of Al(III)

By following similar dilution method, solution of different concentrations 10 mg/L, 20 mg/L, 40 mg/L, 50 mg/L, 75 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, 400 mg/L and so on were prepared in 0.1 N nitric acid solution.

#### **5.1.5 5 N Sulphuric Acid ( $H_2SO_4$ ) Solution**

5 N  $H_2SO_4$  solution was prepared by dissolving 34.72 ml of concentration of conc.  $H_2SO_4$  in 250 ml volumetric flask with distilled water.



### **5.1.6 5 M Nitric Acid (HNO<sub>3</sub>) Solution**

5 M HNO<sub>3</sub> solution was prepared by diluting 78.12 ml of conc. HNO<sub>3</sub> solution in 250 ml volumetric flask with distilled water.

### **5.1.7 5 M Sodium Hydroxide (NaOH) Solution**

5 M NaOH solution was prepared by diluting 50 gm NaOH in 250 ml volumetric flask with distilled water.

### **5.1.8 Preparation of 0.25% 1, 5 Diphenylcarbazide [CO(NHNHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] Solution**

0.25 gm of DPCI was transferred into 100 ml volumetric flask and 50 ml of pure acetone was added slowly with constant stirring in order to ensure complete dissolution of DPCI crystal. Then 50 ml water was added up to the mark. The solution was tightly wrapped with black paper due to high sensitivity of the solution to the light. Fresh solution was prepared when solution turned faint red.

### **5.1.9 Preparation of 0.2% of Eriochrome Cynine R [C<sub>23</sub>H<sub>15</sub>Na<sub>3</sub>O<sub>9</sub>S] Solution**

200 mg of ECR crystal were dissolved in 100 ml volumetric flask in distilled water.

### **5.1.10 Preparation of Buffer Solutions**

Buffer solutions of pH 4.0, pH 7.0, pH 9.2 were prepared by dissolving buffer tablets of pH 4.0, pH 7.0 and pH 9.2 respectively in 100 ml conical flask in distilled water.

## **5.2 Preparation of Adsorbent from Sugarcane Bagasse (SCB)**

### **5.2.1 Preparation of Adsorbent form Raw Sugarcane Baggase (RSCB)**

Raw sugarcane bagasse (RSCB) was collected from sugar mill located at Panga, Kirtipur. This raw bagasse was cleaned with distilled water and dried under sunlight for 2 to 3 days and grinded in mechanical grinder at Central Department of Chemistry, Kirtipur and sieved into mess sizes of 225 µm. Thus obtained raw bagasse has lesser efficacy for the removal of Cr (VI) and Al(III) metal. In order to enhance metal uptake capacities of RSCB, it was then subjected to chemical modification.

### **5.2.2 Preparation of Charcoal from Raw Sugarcane Bagasse (*Saccharum officinarum*)**

Biosorbents are the biomass materials having effective adsorption capabilities. The adsorption efficiency of such agricultural waste can be enhanced by various methods such as steam activation, thermal activation, chemical activation, chemical modification and so on. The organic constituents of such agricultural wastes are chiefly cellulose, hemicelluloses and lignin and other low molecular weight compounds.

Sugarcane bagasse consists of cellulose (50%), hemicellulose (27%) and lignin (23%). The presence of these three biological polymers causes SCB rich in hydroxyl, carbonyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties. Raw sugarcane bagasse was chemically modified by using conc.  $H_2SO_4$  at lab temperature. The bagasse was mixed with conc.  $H_2SO_4$  in (1:2) (w/v) ratio of adsorbent weight to conc.  $H_2SO_4$  and allowed to leave for 24 hours to ensure complete reaction. The excess acid was removed by washing it with distilled water until pH of the filtrate approaches to 7 and then dried at  $100^\circ C$  for 6-8 hours in an oven and sieved to the particle of size  $225\ \mu m$ .<sup>12</sup>

Chemical modification in generally improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion exchange properties, increase in concentration and or formation of new functional groups take place that favours the metal uptake. So by chemical modification of RSCB, the effective surface area of carbon increases and surface of the adsorbent get modified due to the reduction of low molecular weight lignin and decrease in crystallinity of hemicelluloses. This causes increase in concentration and or formation of new functional groups and active sites at the surface of the adsorbents.<sup>38</sup>

### Modification of Raw Sugarcane Bagasse Adsorbent

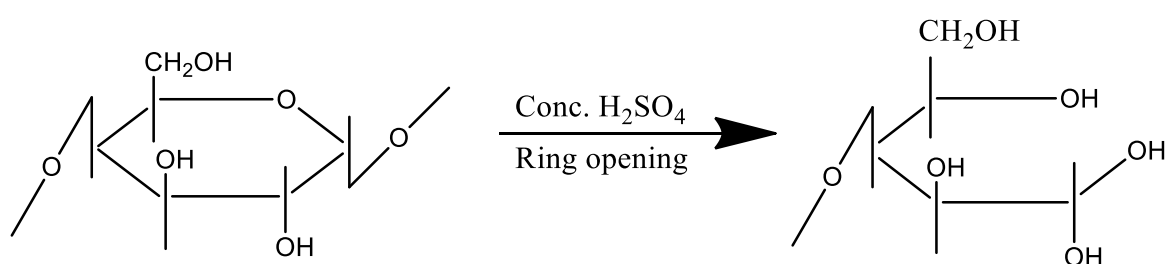


Figure ii: Schematic representation for the ring opening of monomeric unit of cellulose contained in sugarcane waste by treatment with conc.  $H_2SO_4$

## 5.3 Determination of Calibration Curve of Metal Ion Solution

### 5.3.1 Determination of Cr(VI)

0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 ml of working Cr (VI) solution of 5 mg/L were taken in a different 25 ml volumetric flask and was acidified with 1 ml of 5 N  $H_2SO_4$  in each volumetric flask and shaken well. Then 1ml of 0.25% DPCI solution was added to each volumetric flask and shaken well. The volume was then made up to the mark by adding distilled water.

The absorption spectra of red-violet colored Cr(VI)-diphenylcarbazide complex was recorded in Perkin-Elmer spectrophotometer against reagent blank.

At  $\lambda_{\max}$  absorbance of all the solutions were measured against reagent blank using the same spectrophotometer.

### **5.3.2 Determination of Al(III)**

0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 ml of working Al (III) solution of 5 mg/L were taken in different 25 ml volumetric flask and to this 5 ml of pH 6.0 buffer and 1 ml of 0.20% of Eriochrome Cynine R solution was kept and shaken. The volume was then made up to the mark with distilled water.

After 15 min the absorption spectra of pink-purple colored Al (III)-ECR complex was recorded in the same spectrophotometer against reagent blank. At  $\lambda_{\max}$  the absorbance of all the solution were measured against reagent blank using spectrophotometer.

## **5.4 Adsorption Study**

### **5.4.1 Batch Adsorption Studies**

The adsorption of Cr (VI) and Al (III) ion were studied by carrying out batch tests. Synthetic working solutions of Cr (VI) and Al (III) of predetermined concentration and adsorbent prepared from sugarcane bagasse in its raw form as well as in modified form were used. The pH of the solutions were adjusted by using a series of 1M, 2M, 3M, 4M and 5M HNO<sub>3</sub> solutions and series of 1M, 2M, 3M, 4M and 5M NaOH solutions.

The working solutions of various required concentrations of Cr(VI) and Al(III) ion ranged from 50 mg/L to 500 mg/L were prepared by diluting 1000 ml stock solution, where as solution of concentration less than 50 mg/L were prepared by diluting 50 mg/L of working solutions. 25 ml of Cr(VI) and Al(III) solutions of known initial concentration were added to 25 mg of raw and modified sugarcane bagsse in different 125 ml reagent bottles and the mixtures were agitated on a mechanical shaker for 24 hours at laboratory temperature. At the end of the experiment the equilibrated solutions were filtered using filter paper and the filtrates were used to analyze the residual concentration of metal ions. Concentration before and after was determined by using the same spectrophotometer at  $\lambda_{\max}$  540 nm following diphenylcarbazide method for Cr(VI) ion solution and at  $\lambda_{\max}$  530 nm following Eriochrome cynine R method for Al(III) ion solution respectively.

### **5.4.2 Batch pH Studies**

Batch pH studies were conducted by shaking 25 ml of 20 mg/L of Cr(VI) and Al(III) solutions with 25 mg of adsorbents for 24 hours at laboratory temperature. The initial pH of Cr (VI) and Al(III) solutions were adjusted from 1.0 to 7.0 pH values using digital pH meter. Both Cr (VI) and Al(III) samples were shaken in 125 ml reagent bottles using mechanical shaker at laboratory temperature separately. The equilibrium pH of the reaction mixture were recorded and filtrates were used for

remaining Cr(VI) and Al(III) metal ion concentration. The pH at which maximum adsorption of metal ion occurs was selected as optimum pH for the further studies.

#### **5.4.3 Effect of Metal Ion Concentration (Adsorption Isotherm)**

Adsorption isotherm studies were carried out with different initial concentration of Cr(VI) and Al(III) ion ranging from 10 mg/L to 400 mg/L separately with adsorbent dose of 25 mg. The sample solutions were taken in 125 ml reagent bottles and shaken in a mechanical shaker for 24 hours. Both raw sugarcane bagasse (RSCB) and modified sugarcane bagasse (MSCB) were used at optimum pH. The optimum pH for Cr (VI) was 1.0 and that for Al(III) was 6.0 respectively. The remaining metal ion concentrations were determined after filtering the reaction mixture by using the same spectrophotometer. The experiment, regarding adsorption isotherm helps in determining nature of adsorption and maximum adsorption capacity of the adsorbent used.

#### **5.4.4 Batch Equilibrium Time Studies**

The effect of contact time was studied at room temperature at optimum pH. The equilibrium time of the adsorbent for Cr(VI) and Al(III) were investigated at their respective pH values by taking 25 ml of 20 mg/L concentration of Cr(VI) and Al(III) solution in 125ml reagent bottles with 25 mg adsorbent dose. The mixtures were shaken in a mechanical shaker for 10, 20, 30, 40, 50, 60, 80, 100, 120 mins, 3 hr, 4 hr, 6 hr, 10 hr, 12 hr and 24 hr respectively. The metal ion concentration before and after adsorption were determined by spectrophotometer.

#### **5.4.5 Batch Kinetic Studies**

The measurement of adsorption kinetics were carried out at optimum pH for both Cr(VI) and Al(III) separately. 25 ml of 20 mg/L of metal ion solutions were added in different 125 ml reagent bottles containing 25 mg of adsorbent and the mixtures were shaken in a mechanical shaker up to desired contact time. Samples were filtered through filter paper and concentration before and after adsorption were determined spectrophotometrically. The data thus obtained were tested with pseudo-first order, pseudo-second order and second order kinetics.

### **5.5 Characterization of the Charcoal**

#### **5.5.1 Surface Area Determination**

The surface area of sugarcane bagasse was determined by chemical adsorption technique. For the determination of surface area, 0.5 g of raw and modified sugarcane bagasse was agitated with 2.5 ml of different concentration of acetic acid for 120 mins. The final (equilibrium concentration) concentration of acetic acid was determined by titrating with 0.1 N standardized NaOH solution. From the amount of acetic acid adsorbed, specific surface area of the charcoal was determined by the procedure given by BET single point method.

### **5.5.2 Scanning Electron Microscopy (SEM) Image**

Scanning Electron Microscopy (SEM) is a type of electron microscope that images the surface topography of the sample by scanning it with a beam of electrons in a raster scan pattern. SEM image demonstrates the irregular and porous structure of the sugarcane bagasse. SEM image of raw and modified adsorbent were taken by JEOL instrument from Department of Chemistry, Lucknow University, Lucknow, India.

### **5.5.3 Infrared Spectroscopy (IR) Analysis**

Infrared Spectroscopy (IR) technique is mainly used to identify the different functional groups like carboxyl, carbonyl, phenolic etc that are capable of metal uptake. The IR spectra of raw and modified sugarcane bagasse adsorbent were analyzed using Perkin-Elmer infrared spectrophotometer in nujol medium. The IR spectra of the adsorbent were taken from NAST, Khumaltar, Kathmandu.

### **5.5.4 Titrimetric Method (Boehm Titration)**

In order to quantify surface functional group of sugarcane bagasse modified charcoal, Boehm titration procedure was employed. For this 250 mg of adsorbent was agitated with 50 ml of 0.02 N bases namely  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{NaOH}$  and 0.02 N  $\text{HCl}$  in mechanical shaker for 48 hours. The mixture was then filtered and 5 ml of this filtrate was titrated with 0.02N  $\text{HCl}$  or  $\text{NaOH}$  using phenolphthalein or methyl orange indicator. On the basis of volume of acid or base consumed by the definite weight of charcoal, the amount of oxygen containing functional group per gram charcoal is calculated following the Boehm's titration.

Both acidic as well as basic functional groups were quantified by means of titrimetric technique developed from Boehm's work. According to Boehm's assumptions: <sup>15</sup>

- (i)  $\text{NaHCO}_3$  neutralizes carboxyl group only,
- (ii)  $\text{Na}_2\text{CO}_3$  neutralizes carboxyl and lactone groups and
- (iii)  $\text{NaOH}$  neutralizes carboxyl, lactone and phenolic groups.

## **6. Results and Discussion**

### **6.1 Absorption Spectra and Calibration Curve for Cr(VI) and Al(III)**

#### **6.1.1 Calibration Curve for Cr(VI) Complex with DPCI**

Extensive literature reviews indicate that in the absence of acid there is no formation of colored complex between Cr(VI) and DPCI. So 1 ml of 5N H<sub>2</sub>SO<sub>4</sub> solution was added in 25 ml final solution as the acid has positive impact in the formation of intense red-violet color of Cr(VI)-diphenylcarbazide. The nature of the absorption spectra and  $\lambda_{\text{max}}$  obtained at 540 nm match with the reported values.<sup>33</sup>

The absorption spectra of the red-violet coloured complex of Cr (VI)-diphenylcarbazide and the calibration curve for the Cr (VI) )- diphenylcarbazide are shown in figures 1 and 2.

#### **6.1.2 Calibration curve for Al(III) complex with ECR**

In solution state Al occurs in +3 oxidation state between pH 4 and 9. Beyond this pH its hydroxide gets precipitated. With the ligand ECR, Al forms a complex of pink- purple colour. Aluminium as Al(III) starts to form hydroxide compounds at pH 3.5 and there is a mixture of Al(OH)<sub>2</sub> and Al(OH)<sub>3</sub> which leads a rapid formation of insoluble Al(OH)<sub>3</sub> above pH 6.<sup>25</sup> The nature of the absorption spectra and  $\lambda_{\text{max}}$  obtained at 530 nm match with the reported value.<sup>15</sup>

The absorption spectra of the pink-purple coloured complex of Al (III)-ECR complex and the calibration curve for the Al (III)-ECR complex are shown in figures 3 and 4.

### **6.2 Characterization of Charcoal**

#### **6.2.1 Surface Area Determination**

The surface area of the sugarcane bagasse was determined by acetic acid adsorption technique. The surface area of the modified sugarcane bagasse is greatly increased due to the treatment with concentrated sulphuric acid. The surface area of MSCB was calculated to be 357 m<sup>2</sup>/g which was greater than the surface area of RSCB (49 m<sup>2</sup>/g).

#### **6.2.2 Scanning Electron Microscopy (SEM) Image of the Charcoal**

The SEM image of raw and modified charcoal are shown in figures 19 and 20 respectively. The morphological studies clearly revealed that the adsorbent is amorphous and highly porous in nature. It was found that there were holes and caves like openings on the surface of adsorbent which would have more surface area available for adsorption than the raw charcoal.

### 6.2.3 Infrared Spectra Analysis

The IR spectra of raw and modified sugarcane bagasse is shown in figure 21. The IR spectra provide fingerprints of different functional groups present in the adsorbent surface. The mechanism for the adsorption for heavy metals by sugarcane bagasse is linked to the role played by the essential stretching functional groups like hydroxyl (-OH), carboxylic (-COOH), carbonyl (C=O) and other aromatic and phenolic groups.<sup>38</sup> The spectra show that, bands at  $1370\text{ cm}^{-1}$  and  $1440\text{ cm}^{-1}$  are associated to C-O stretching O-H bending modes of phenols and carboxylic acids. Bands nearly at  $3000\text{ cm}^{-1}$  is associated -OH group of phenol, alcohol and carboxylic groups.

### 6.2.4 Titrimetric Method (Boehm Titration)

On the basis of acid or base consumed by the definite weight of charcoal, the amount of oxygen containing functional groups per gram charcoal is calculated following the Boehm's procedure. The result obtained from the Boehm's titration regarding the amount of acidic/basic functional group is presented in table 1.

Table. 1: Results of Boehm's titration

S.N.	Adsorbents	Functional groups milliequivalent per gram (meq/g)			
		Carboxyl	Lactones	Phenols	Basic
I	MSCB	1.5	0.4	0.6	0.3
II	RSCB	0.5	0.1	0.3	0.8

From the above table it is clear that the oxygen containing (acidic) functional groups increase significantly on treating the raw charcoal with sulphuric acid at moderate temperature. It has been found that the acidic and basic surface sites co-exist simultaneously but the concentration of basic sites decrease with increase in acidic character of the surface.<sup>15</sup>

## 6.3 Batch Adsorption Study

### 6.3.1 Batch pH Studies for Cr(VI)

Figure 5 shows the effect of pH on the adsorption of Cr(VI) on RSCB and MSCB at initial concentration of 25 mg/L at lab temperature. The percentage removal of Cr (VI) by MSCB decreased from nearly 95% to 11% when the pH of the solution was increased from 1 to 6. Similarly in case of RSCB the removal percentage decreases from about 35% to 4% when pH is increased from 1 to 6. This shows that adsorption was maximum at pH 1 and adsorption was insignificant at pH 6. Thus the optimal pH for the adsorption of Cr (VI) on these adsorbent was found to be 1.<sup>33</sup>

It has been reported that biomaterials like sugarcane bagasse removes Cr(VI) from aqueous solution through anionic adsorption and partial reduction in to Cr(III).<sup>40,41</sup>

### 6.3.2 Batch pH Studies for Al(III)

Figure 6 shows the effect of pH on the adsorption of Al(III) on RSCB and MSCB at initial concentration of 25 mg/L at laboratory temperature. The percentage

removal of Al(III) increased from 4% to 36% in case of RSCB and from 10% to 88% in case of MSCB with increase in pH from 1 to 6. Beyond pH 6 there is rapid formation of insoluble Al(OH)<sub>3</sub> i.e. rapid precipitation occurs above pH 6. Thus the optimal pH for the adsorption of Al (III) on these adsorbent was found to be 6.<sup>25</sup>

It is believed that most of the metal ions including Al(III) is removed from aqueous solution by cationic mechanism because at higher pH value (greater than 4) binding sites of the adsorbent start deprotonating and the metal uptake becomes difficult.<sup>42</sup>

### 6.3.3 Batch Isotherm Studies

The adsorption isotherms for the adsorption of Cr (VI) and Al(III) on MSCB and RSCB are shown in figures 7 and 8 respectively. The adsorption of Cr(VI) and Al(III) on respective adsorbents increases with increase in time and attained an equilibrium value after some time. Experimentally it was found that concentration ranging from 10 mg/L to 400 mg/L the amount of Cr(VI) adsorbed increases from 7.92 to 131.68 mg/g in case of MSCB and 3.09 to 27.01 mg/g in case of RSCB for 25 mg/L solution at optimum pH 1.0 at lab temperature.

Similarly, for the same range of concentration the amount of Al(III) adsorbed increases from 8.01 to 125.89 mg/g in case of MSCB and 4.13 to 34.24 mg/g in case of RSCB at optimum pH 6.0 at laboratory temperature.

Thus in both cases the obtained results revealed that the adsorption capabilities of MSCB was found to be increased greatly than RSCB, due to chemical modification.

Figures 9, 10, 11 and 12 represent the Langmuir and Freundlich isotherm for the adsorption of Cr(VI) and Al(III), respectively on RSCB and MSCB. Adsorption of Cr(VI) and Al(III) give the linear relationship with Langmuir and Freundlich isotherms. Both Langmuir and Freundlich parameters are determined from the slopes and intercepts of their respective plots and these values are given in tables 2 and 3.

Table. 2: Langmuir and Freundlich parameters for the adsorption of Cr(VI) on MSCB and RSCB

S.N.	Adsorbents	q <sub>m</sub> (exp) (mg/g)	Langmuir Isotherm			Freundlich Isotherm		
			q <sub>m</sub> (mg/g)	b(L/mg)	R <sup>2</sup>	K(mg/g)	1/n	R <sup>2</sup>
i	MSCB	131.68	140	0.036	0.977	8.09	0.541	0.91
ii	RSCB	27.01	33.33	0.018	0.974	1.48	0.552	0.903

Table. 3: Langmuir and Freundlich parameters for the adsorption of Al(III) on MSCB and RSCB

S.N.	Adsorbents	q <sub>m</sub> (exp) (mg/g)	Langmuir Isotherm			Freundlich Isotherm		
			q <sub>m</sub> (mg/g)	b(L/mg)	R <sup>2</sup>	K(mg/g)	1/n	R <sup>2</sup>
i	MSCB	125.89	140	0.037	0.99	9.09	0.507	0.85
ii	RSCB	34.24	38.46	0.0304	0.996	3.31	0.442	0.874



From above two tables it is clear that the value of  $1/n$  is less than unity in respective charcoals which indicates adsorption isotherm is favourable for removal of metal ions. From the table it is also clear that the correlation coefficient ( $R^2$ ) in case of Langmuir adsorption isotherm is greater than Freundlich adsorption isotherm which indicates that adsorption process fits more closely to Langmuir adsorption isotherm model. This shows that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interaction between the adsorbed ions.

### 6.3.4 Batch Kinetics Study

Figures 13, 14, 15, 16, 17 and 18 represent the pseudo-first order, pseudo-second order and second order kinetic models for the adsorption of Cr(VI) and Al(III) on respective adsorbents.

The sorption of Cr(VI) and Al(III) on the respective adsorbents were observed from 10 mins to 24 hours. Initially the adsorption capacity was found to be optimal due to the presence of large number of active sites. After the achievements of active saturation condition in adsorption of Cr(VI) and Al(III) the sorption of the metals become constant. In case of Cr(VI) the saturation condition obtained after 120 mins and 180 mins and in case of Al(III) the saturation condition was obtained after 120 mins.

The values of correlation coefficients and graphical plots clearly showed that the pseudo-second order kinetic model best describes the kinetic data with higher  $R^2$  values than the other models. The amount of adsorption  $q_e$  (mg/g) of Cr(VI) and Al(III) on the respective adsorbents obtained from the experiments were close to the  $q_e$  (mg/g) value obtained from the pseudo-second order plot. So, it is concluded that the adsorption of Cr(VI) and Al(III) followed the pseudo-second order kinetic model. The best fitting of kinetic data to pseudo-second order implies that both Cr(VI) and Al(III) adsorption occur in a monolayer fashion and adsorption pattern occurs through chemical adsorption or ion exchange. The value of correlation coefficient and rate constants are shown in tables 4 and 5 for Cr(VI) and Al(III), respectively.

Table. 4: Pseudo-first order and Pseudo-second order rate constant for the adsorption of Cr(VI) onto MSCB and RSCB

S.N.	Adsorbents	Pseudo-first order		Pseudo-second order		
		$K_1$ (L/min)	$R^2$	$K_2$ (g/mg.min)	$h$ (mg/g.min)	$R^2$
i	MSCB	$2.07 \times 10^{-2}$	0.888	$3.76 \times 10^{-4}$	0.275	0.95
ii	RSCB	$2.072 \times 10^{-2}$	0.875	$9.06 \times 10^{-4}$	0.11	0.974

Table. 5: Pseudo-first order and Pseudo-second order rate constant for the adsorption of Al(III) onto MSCB and RSCB

S.N.	Adsorbents	Pseudo-first order		Pseudo-second order		
		$K_1$ (L/min)	$R^2$	$K_2$ (g/mg.min)	$h$ (mg/g.min)	$R^2$
I	MSCB	$1.842 \times 10^{-2}$	0.858	$3.08 \times 10^{-4}$	0.237	0.97
Ii	RSCB	$1.38 \times 10^{-2}$	0.867	$5.79 \times 10^{-4}$	0.12	0.931

### Plausible Adsorption Mechanism of Cr(VI) onto the Adsorbent

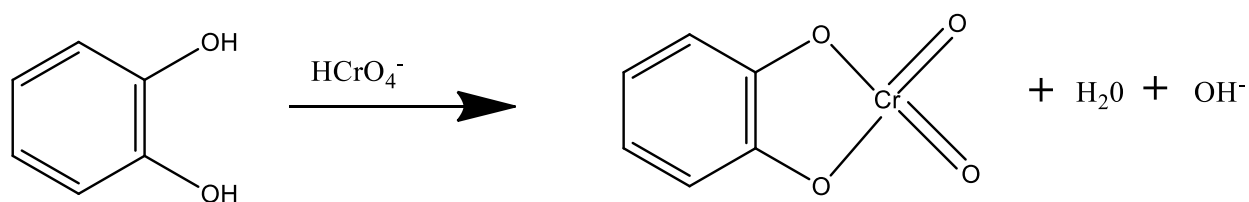
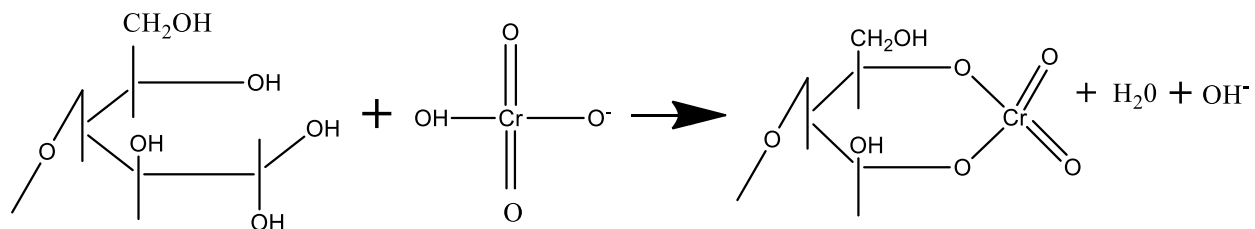


Figure iii: Complexation of Cr(VI) with Polyphenolic/ Polyhydroxyl functional moiety of sugarcane waste

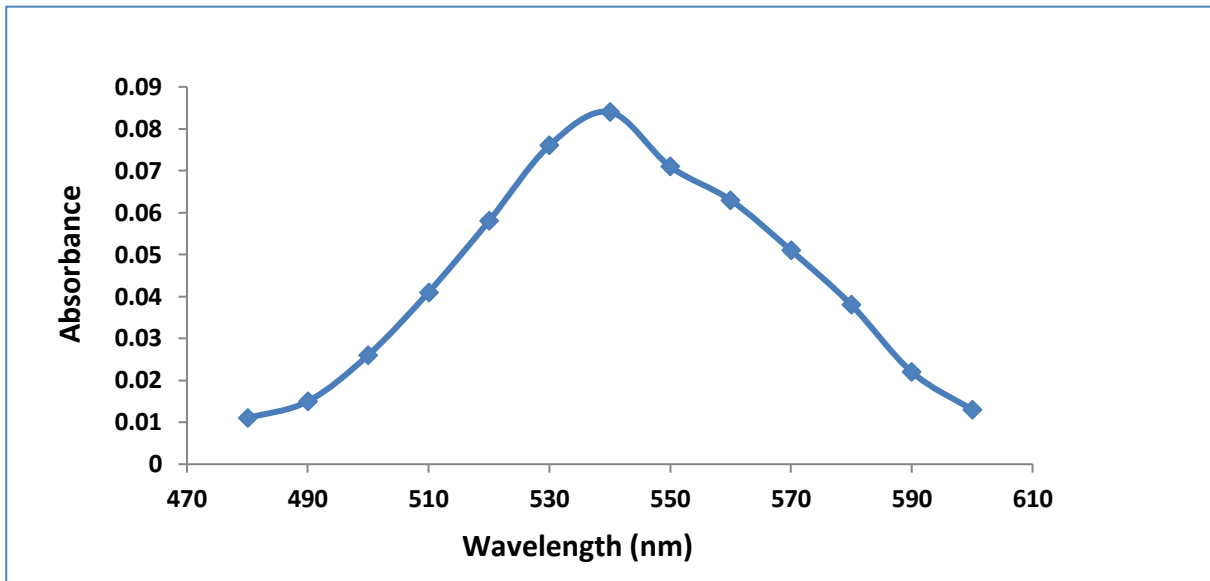


Figure 1: Plot of absorbance against wavelength for determination of  $\lambda_{\max}$  for Cr(VI)

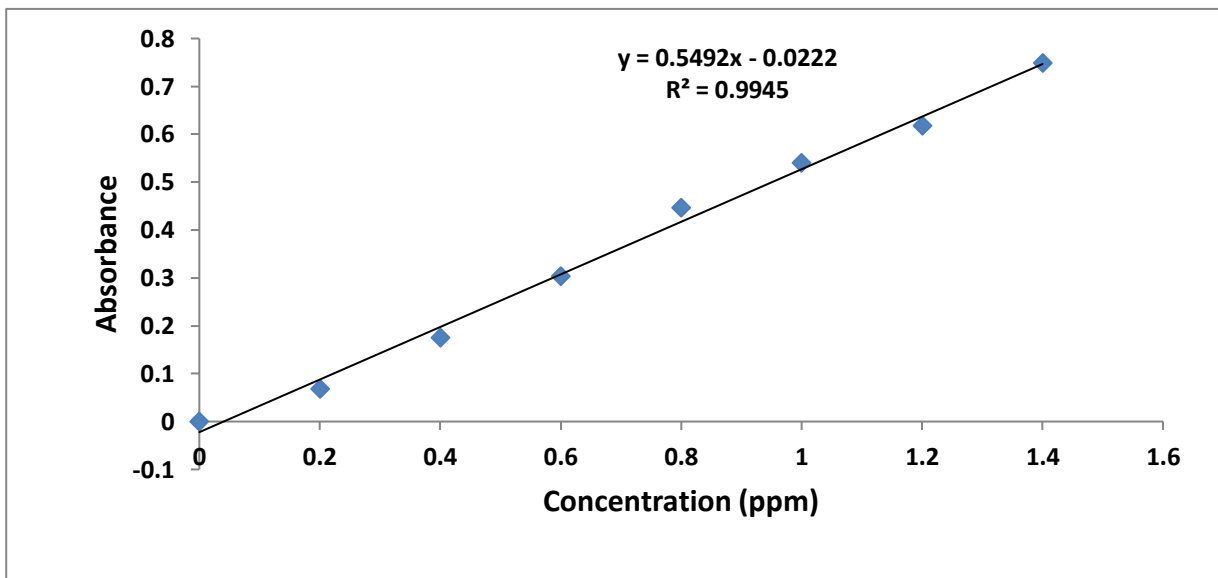


Figure 2: Calibration curve for Cr(VI)

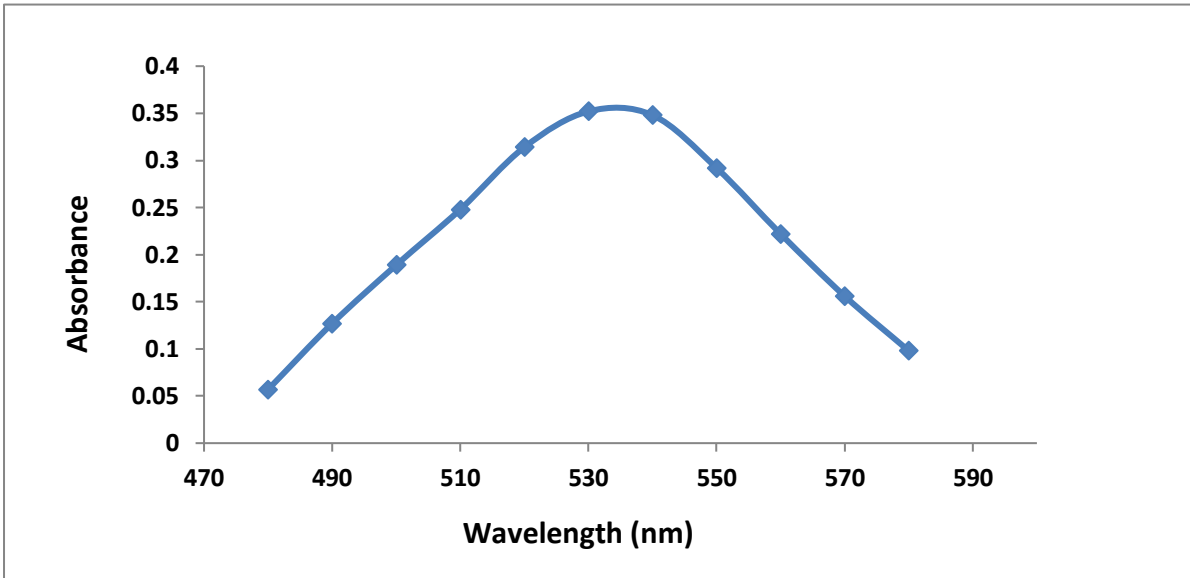


Figure 3: Plot of absorbance against wavelength for determination of  $\lambda_{\max}$  for Al(III)

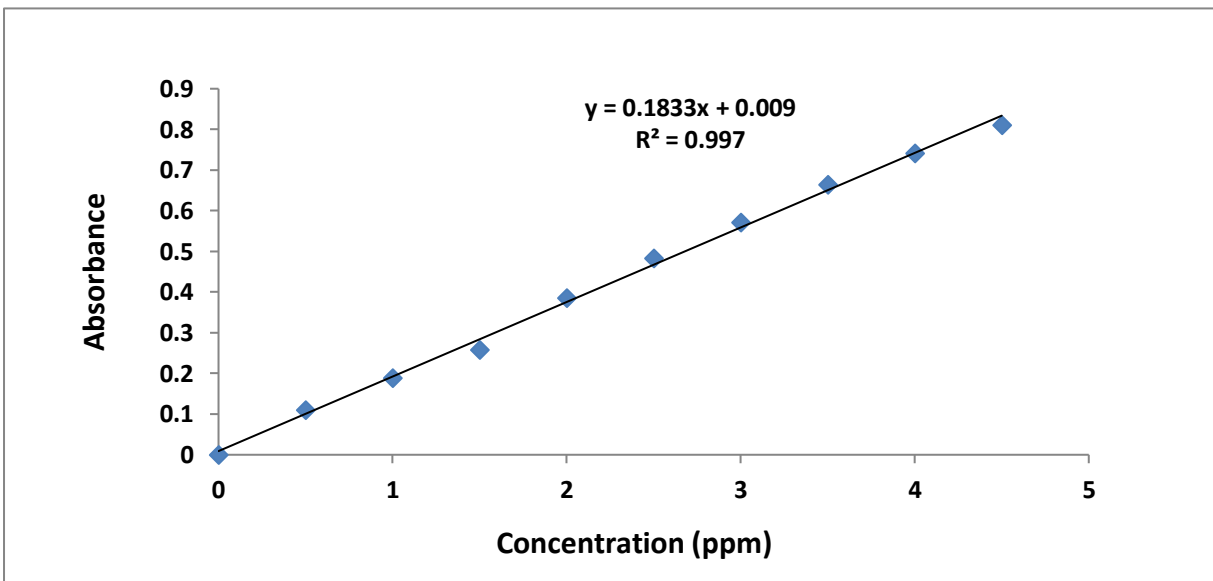


Figure 4: Calibration curve for Al(III)

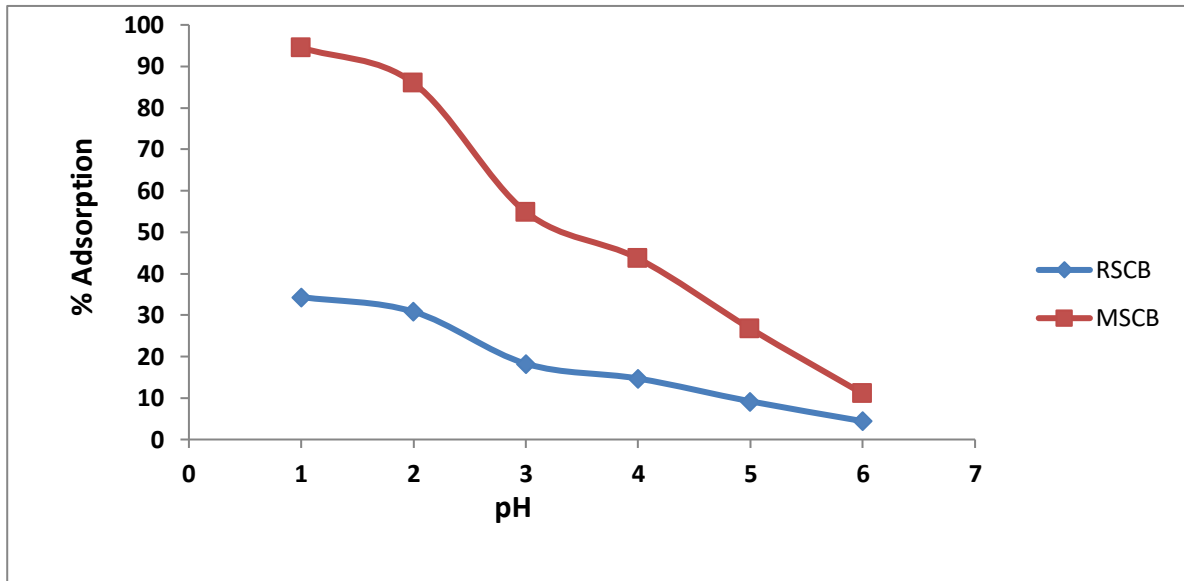


Figure 5: Effect of pH on removal of Cr(VI) by RSCB and MSCB

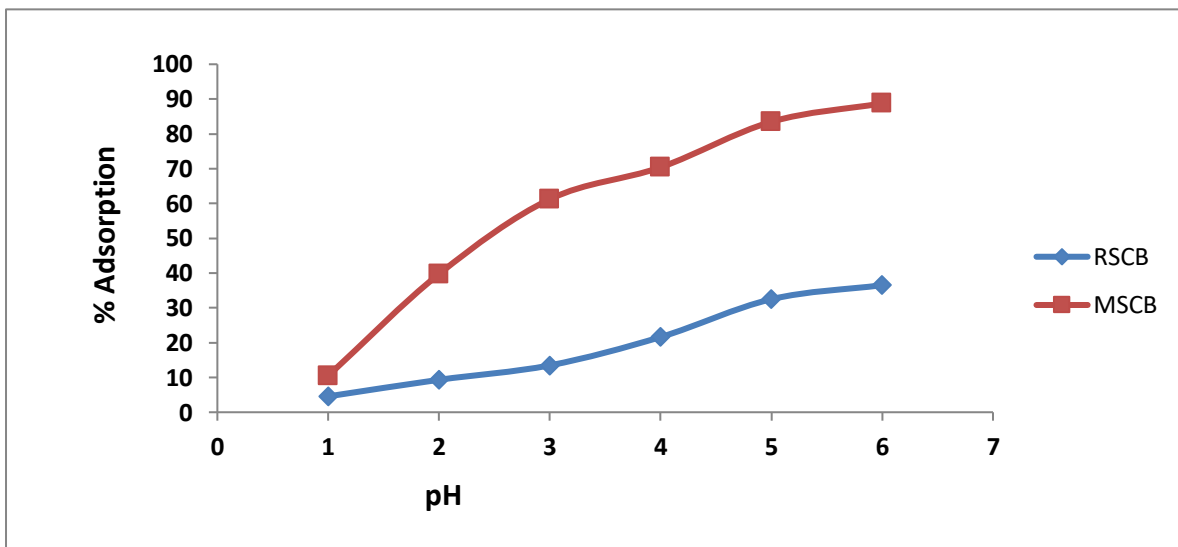


Figure 6: Effect of pH on removal of Al(III) by RSCB and MSCB

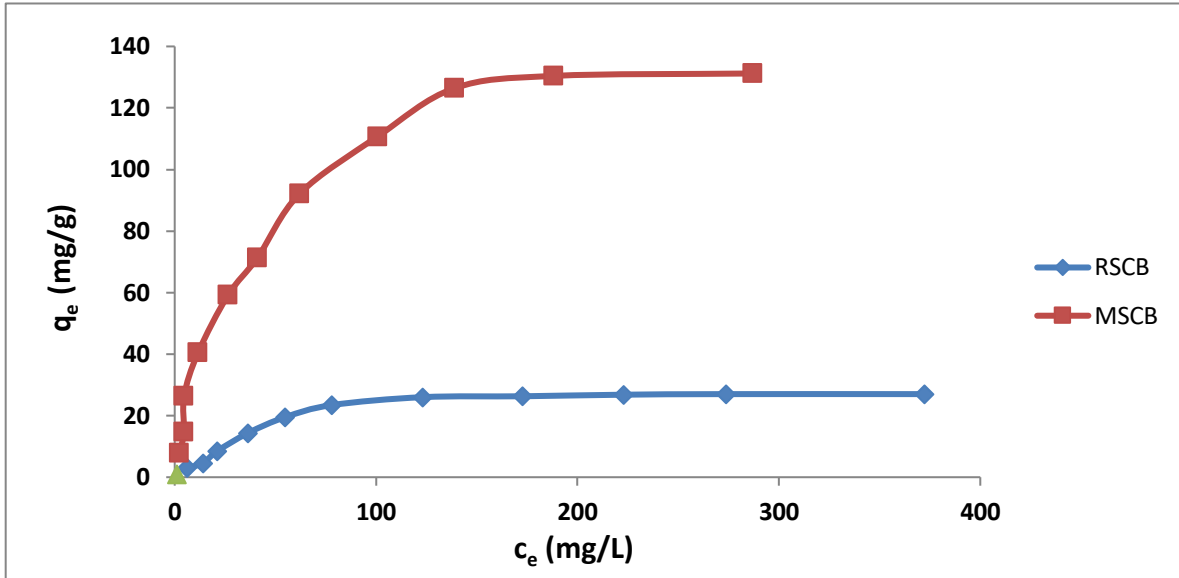


Figure 7: Adsorption isotherm for adsorption of Cr(VI) onto RSCB and MSCB

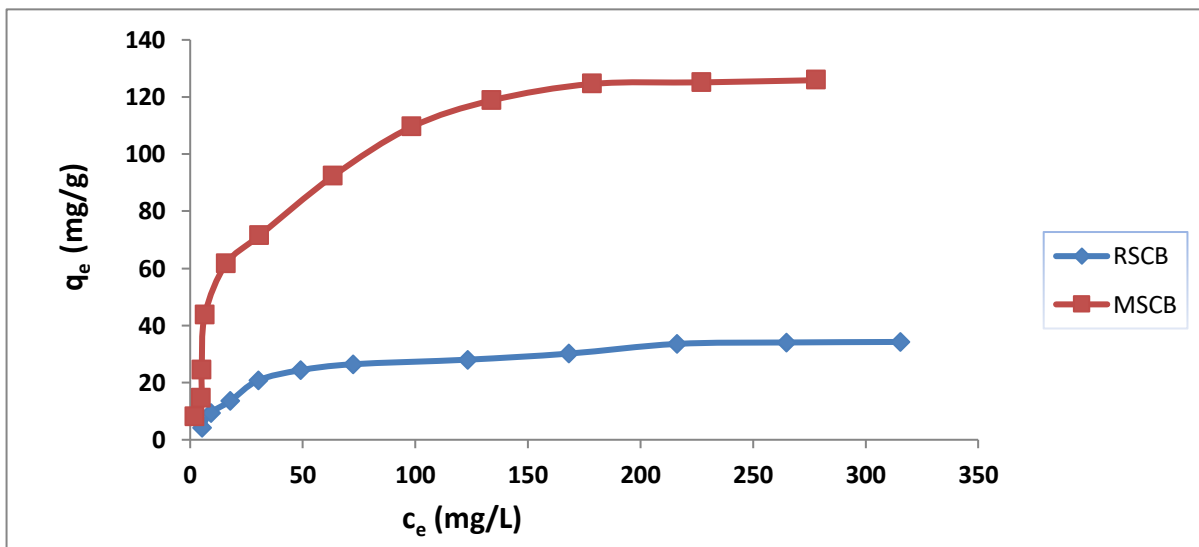


Figure 8: Adsorption isotherm for adsorption of Al(III) onto RSCB and MSCB

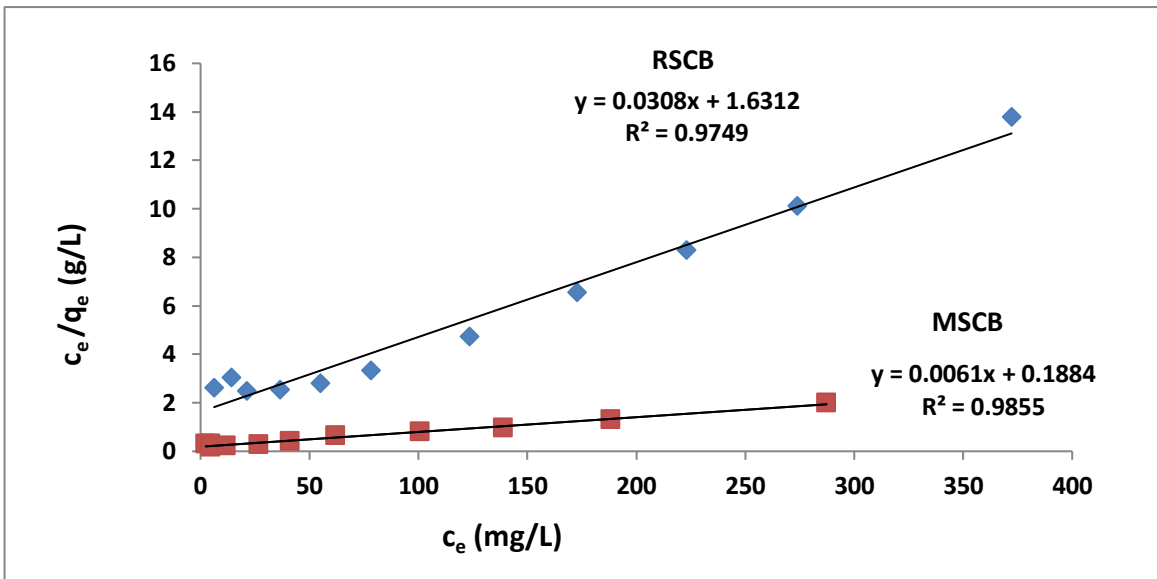


Figure 9: Langmuir isotherm plot for adsorption of Cr(VI) onto RSCB and MSCB

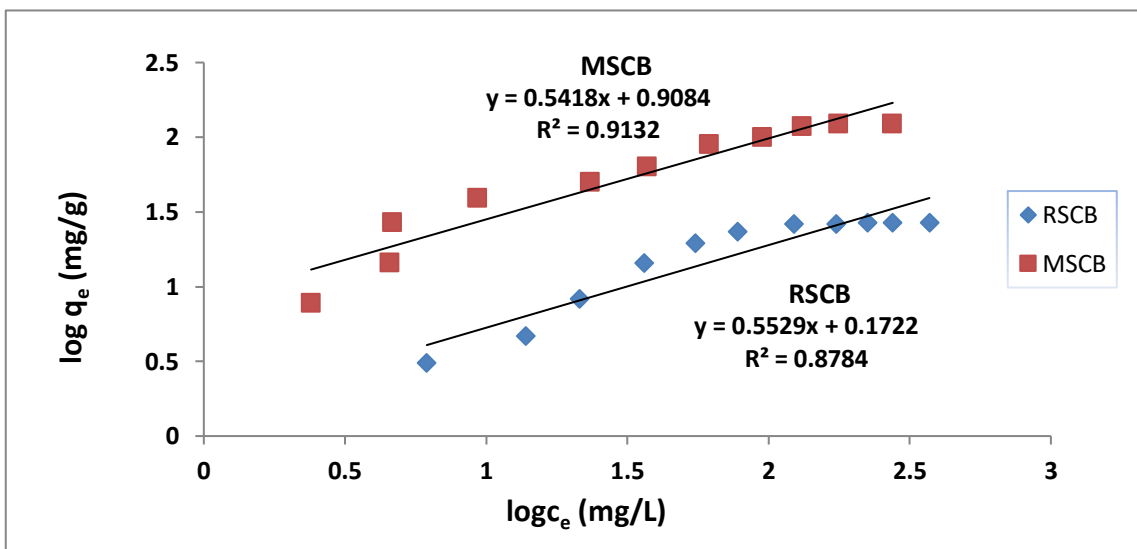


Figure 10: Freundlich isotherm plot for adsorption of Cr(VI) onto RSCB and MSCB

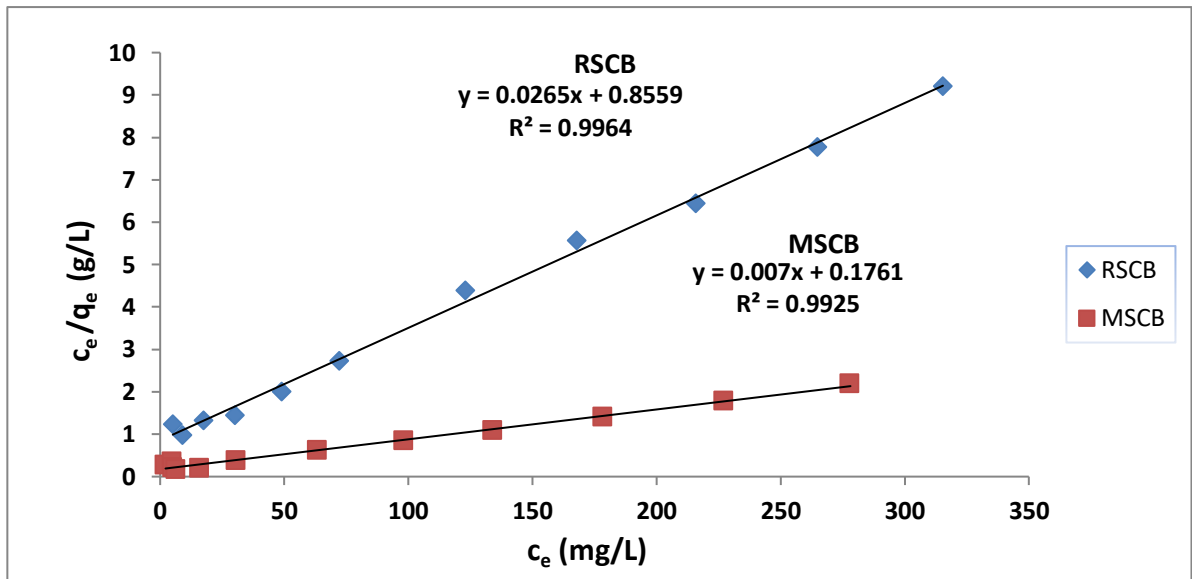


Figure 11: Langmuir isotherm plot for adsorption of Al(III) onto RSCB and MSCB

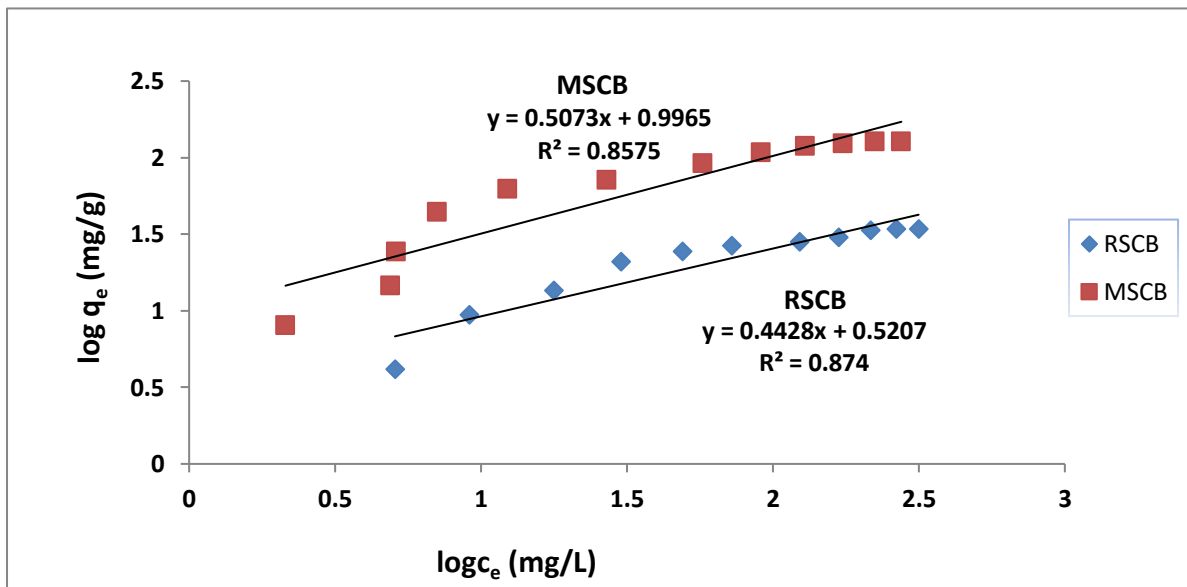


Figure 12: Freundlich isotherm plot for adsorption of Al(III) onto RSCB and MSCB



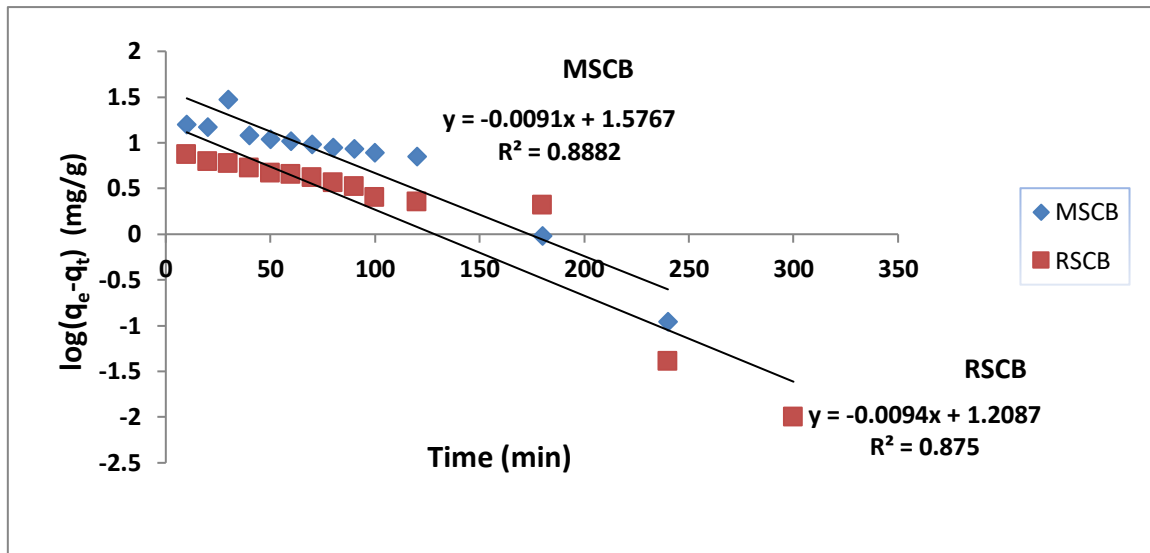


Figure 13: Pseudo-first order kinetic plot for adsorption of Cr(VI) onto RSCB and MSCB

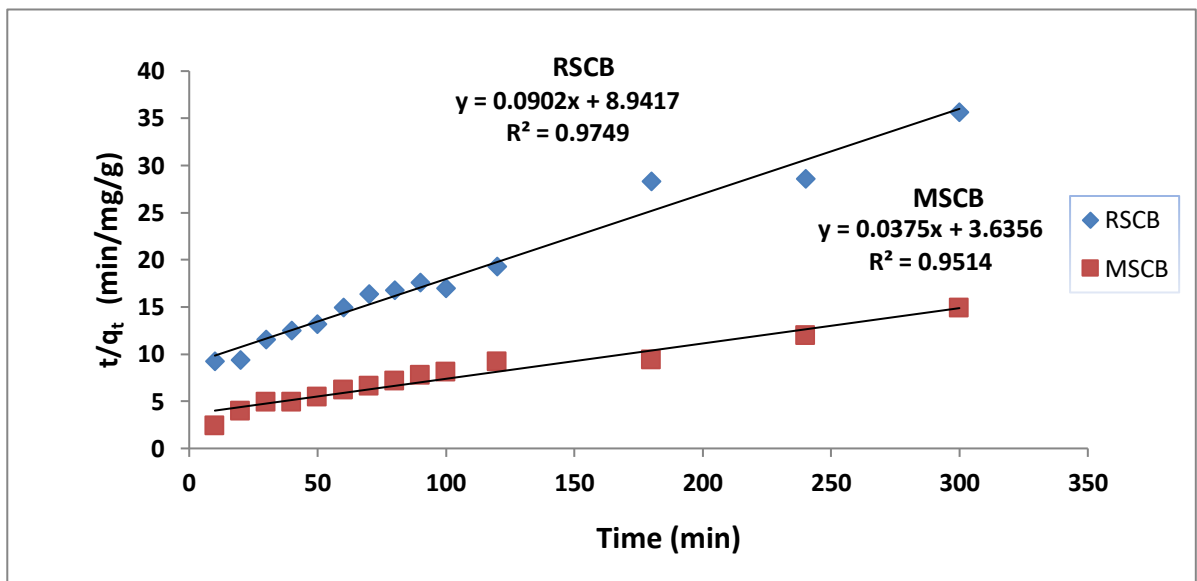


Figure 14: Pseudo-second order kinetic plot for adsorption of Cr(VI) onto RSCB and MSCB

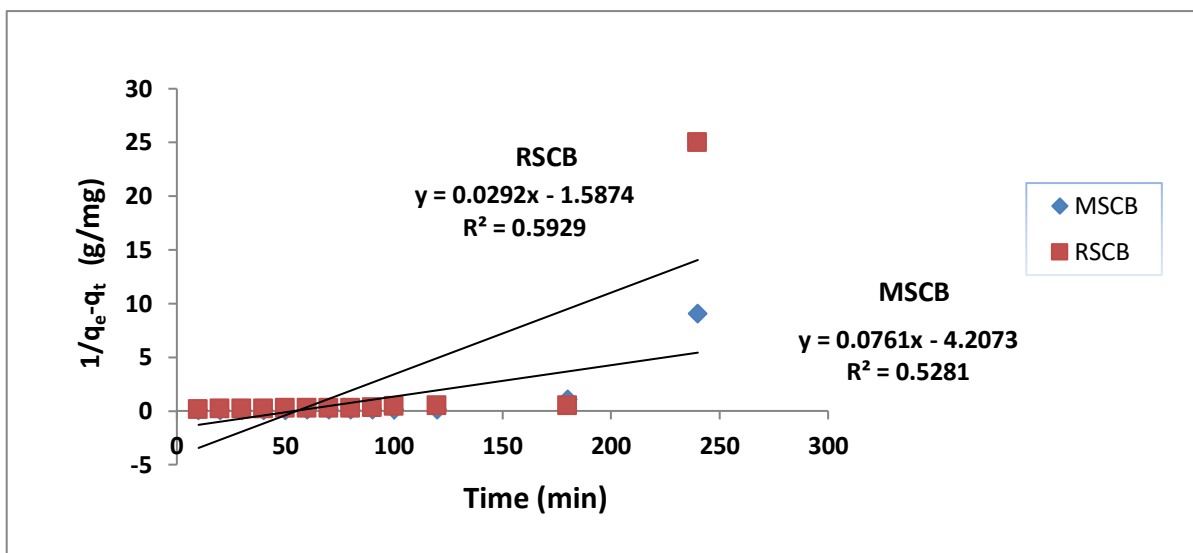


Figure 15: Second order kinetic plot for adsorption of Cr(VI) onto RSCB and MSCB

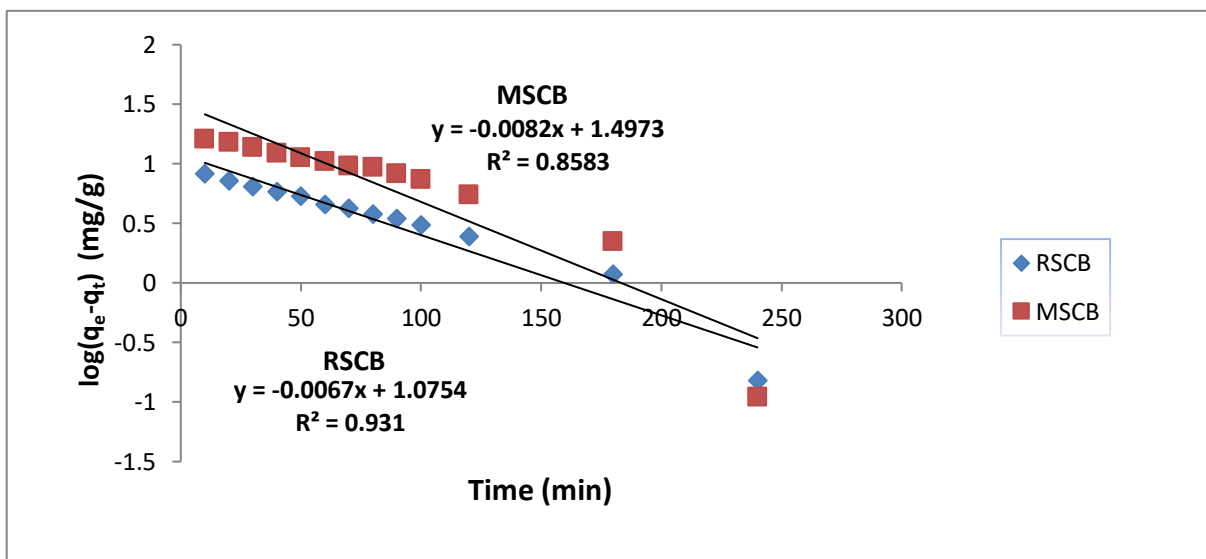


Figure 16: Pseudo-first order kinetic plot for adsorption of Al(III) onto RSCB and MSCB

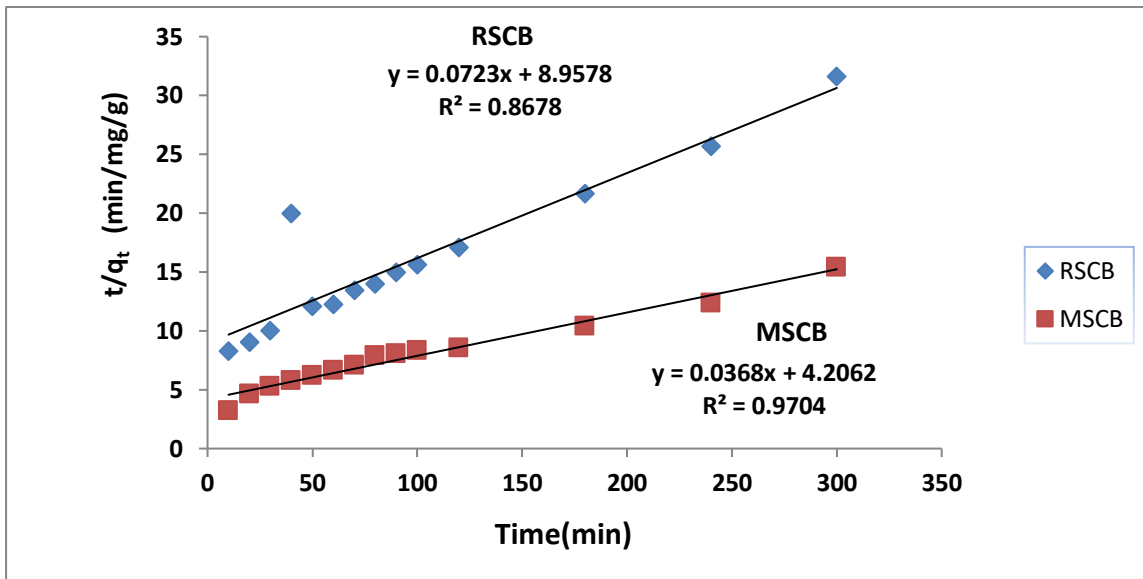


Figure 17: Pseudo-second order kinetic plot for adsorption of Al(III) onto RSCB and MSCB

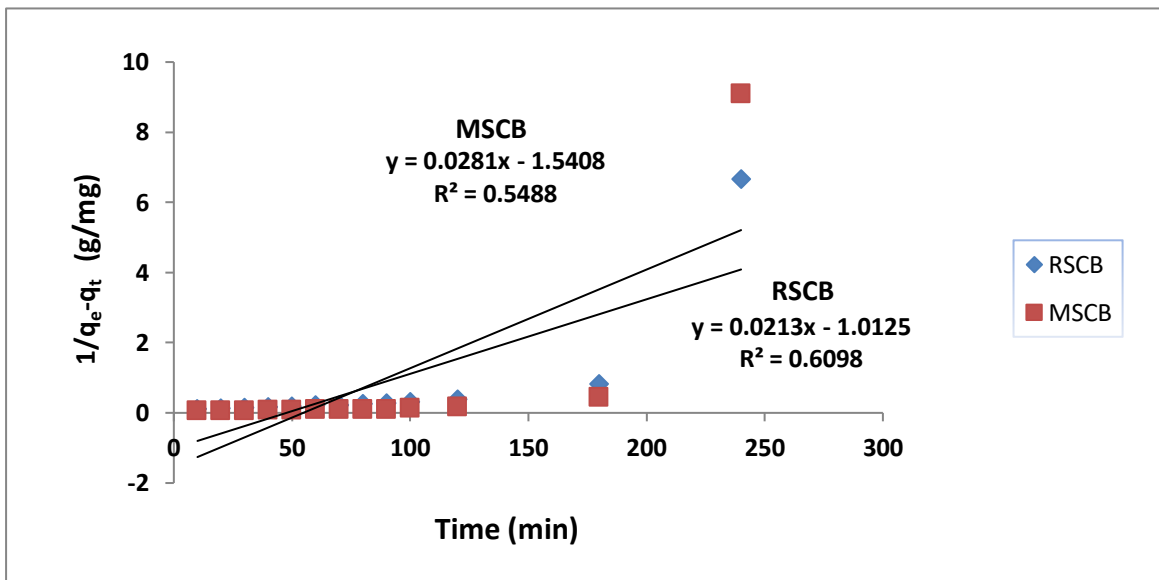


Figure 18: Second order kinetic plot for adsorption of Al(III) onto RSCB and MSCB

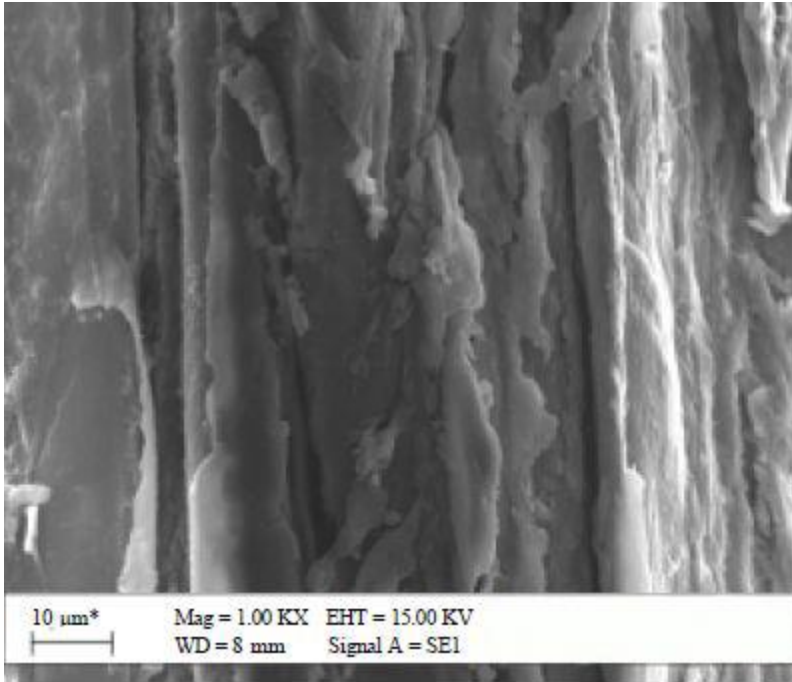


Figure 19: SEM image of RSCB

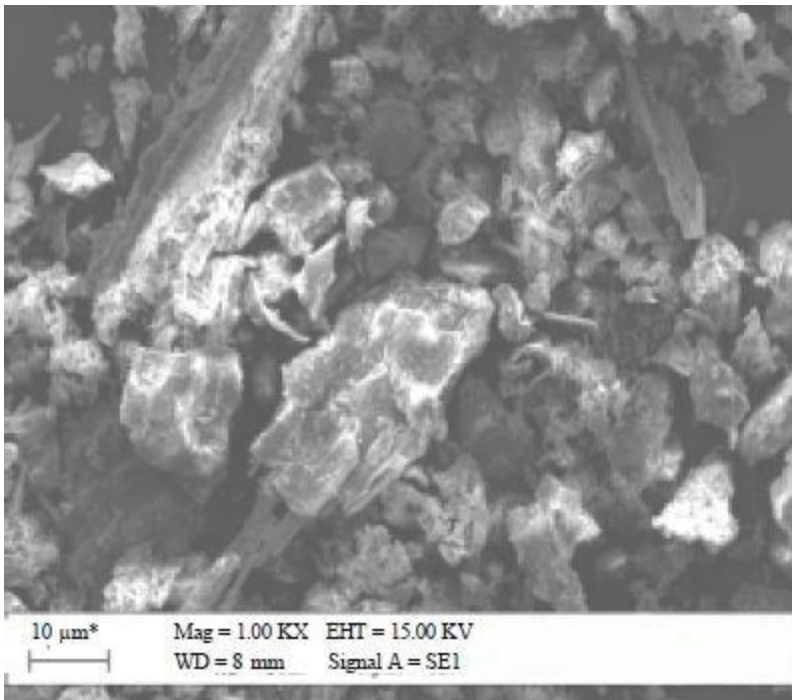


Figure 20: SEM image of MSCB

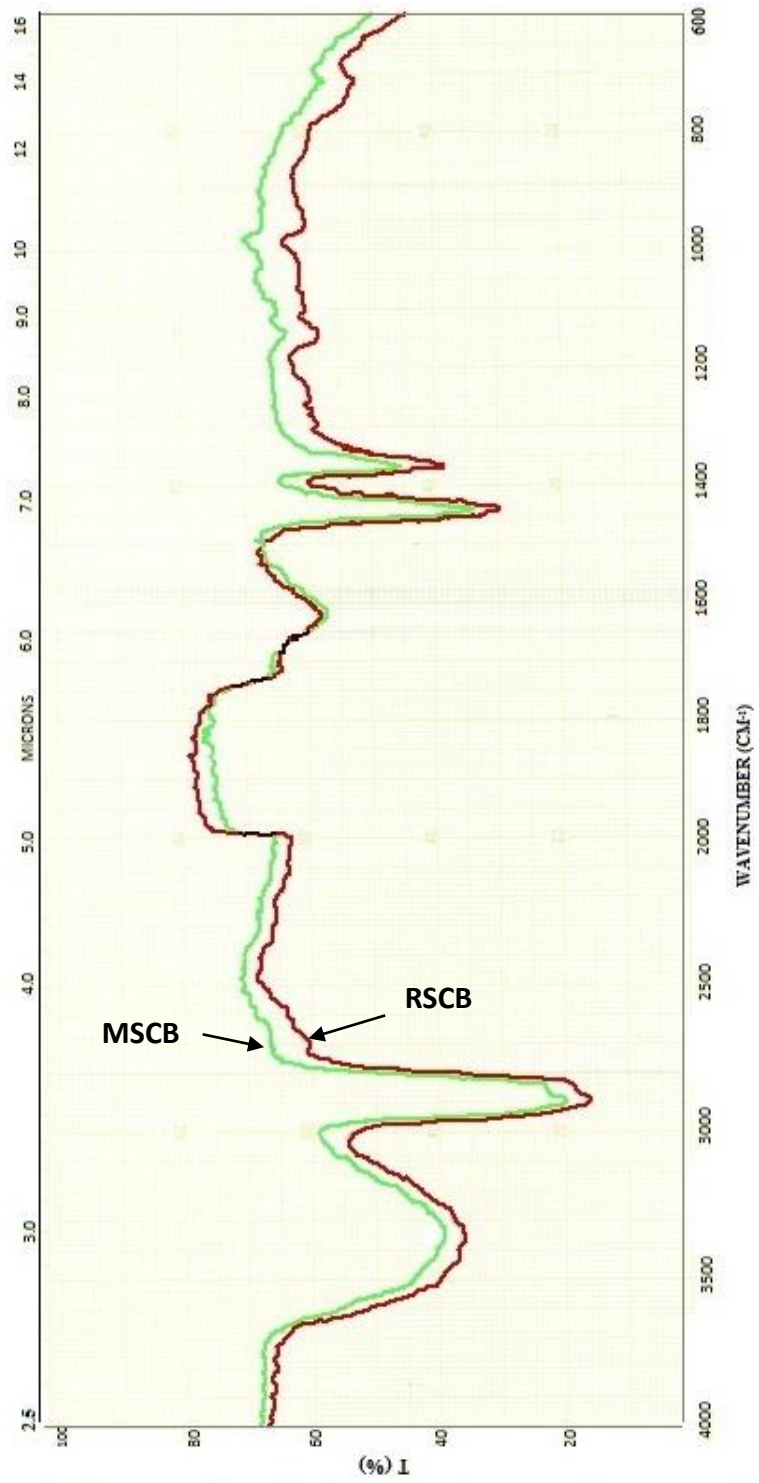


Figure 21: IR spectra of RSCB and MSCB

## 7. Conclusion

The excessive release of heavy metals into the environment is a major concern worldwide. Adsorption process is one of the most suitable technique for the removal of heavy metals from waste water and activated carbon has been widely used as an adsorbent. Sugarcane bagasse, which is abundantly accessible low-cost agricultural waste in Nepal, can be easily converted to carbonaceous material by chemical treatment with concentrated sulphuric acid ( $H_2SO_4$ ). This treated sugarcane bagasse can act just like commercial activated carbon for the metal removal by adsorption phenomena. The surface area of the sugarcane bagasse charcoal after chemical treatment had increased greatly and was found to be  $357\text{ m}^2/\text{g}$ .

The chemically modified sugarcane bagasse charcoal has been found to be an efficient adsorbent for the removal of Cr(VI) and Al(III) from the aqueous solution than using the untreated raw sugarcane bagasse. The adsorption behaviour was dependent on the pH of the system, initial concentration of the adsorbate and the contact time as well.

From the study, it was observed that the maximum adsorption of Cr(VI) and Al(III) on to these adsorbents took place at optimal pH 1.0 and 6.0 respectively. The maximum adsorption capacity of Cr(VI) on modified sugarcane bagasse charcoal and raw sugarcane bagasse charcoal was found to be  $131.68\text{ mg/g}$  and  $27.01\text{ mg/g}$  respectively at their optimal pH 1.0. Similarly the maximum adsorption capacity of Al(III) on modified sugarcane bagasse charcoal and raw sugarcane bagasse was found to be  $125.89\text{ mg/g}$  and  $34.24\text{ mg/g}$  respectively at the optimal pH 6.0. Both the Langmuir and Freundlich adsorption isotherms were tested to describe the adsorption process. It is concluded that Langmuir adsorption isotherm model is found to be more applicable than Freundlich adsorption isotherm for the better description on the adsorption behaviour of Cr(VI) and Al(III) metal ions.

The equilibrium time for Cr(VI) is found to be 180 min and the equilibrium time for Al(III) is found to be 120 min. The experimental data were fitted with pseudo first-order, pseudo second-order and the second order model. It was found that pseudo second order model provides a best descriptive to experimental data.

Characterization of adsorbent was performed by determining surface area of the charcoal, SEM image and IR spectra analysis and performing Boehm titration. All of these characterizing parameters support well for the efficacious adsorption capacity for Cr(VI) and Al(III) metal ions from aqueous system on modified sugarcane bagasse than raw sugarcane bagasse. Thus sugarcane biomass (*Saccharum officinarum*) can be very effectively used to remove heavy metals from aqueous system and the effectiveness of this biomass can be enhanced by chemical modification.

## References

1. Clement, R. E., Eiceman, G. A., Koester, C. J., *Anal Chem.* 1995, **67**, 22-55.
2. Demirbas, E., Kobaya, M., Senturk, E., Ozkan, T., *Water S. A.*, 2004, **30**, 533-538.
3. *Standard Method for Estimation of Water and Waste Water*, 1998, 20<sup>th</sup> Edition, APHA, AAWA, WEF, USA.
4. Sharma, D. C., Forster, C. F., *Bioresource Technol.*, 1995, **30**, 261-267.
5. Ajmal, M., Rao, R. A. K., Siddiqui, B. A., *Water Research*, 1996, **30**, 1478-1482.
6. Clarke, N., Danielson, L. G., Sparen, A., *Pure and App. Chem.*, 1996, **68**, 1597-1638.
7. Johnson, T. A., Jain, N., Joshi, H. C., Prasad, S., *J. of Scientific and Industrial Research*, 2008, **67**, 647-658.
8. <http://www.aseanenvironment.info/Abstract/43005262>
9. Garg, U. K., Sud, D., *Electron. J. Environ. Agric. Food. Chem.*, 2005, **4**, 1150-1160.
10. Ghorai, S., Pant, K. K., *Separation and Purification Technology*, 2005, **42**, 265-271.
11. Hatim, M. D. I., Fazara, M. A. U., *KUKUM Engineering Research Seminar*, 2006.
12. Demirbas, E., Kobaya, M., Oncel, M. S., Sencom, S., *Bioresor. Technol.*, 2002, **84**, 291-293.
13. Ghimire, K. N., Bohara, K. P., *University Experimental Physical Chemistry*, 2008, 139-154.
14. Febrianto, J., Kosasih, A. N., Sunarso, J. Y., Indraswati, N., Ismadji, S., *J. Hazardous Materials*, 2009, **162**, 616-645.
15. Lamsal, N., *An Unpublished M.Sc. Desertation*, T.U., 2009.
16. Vogel's Text Book of Quantitative Chemical Analysis, 2003, 6<sup>th</sup> Edition, Pearson Education Ltd, 668.
17. Kumar, U., Bandyopadhaya, M., *Bioresource Technology*, 2006, **97**, 104-109.
18. Shah, B. A., Singh, A. V., *Int. J. Environ. Sci Tech.*, 2009, **6**, 77-90.
19. Kadirevelu, K., Thamaraiselvi, K., Namasivayam, C., *Separation and Purification Technology*, 2001, **24**, 497-505.
20. Ong, S. A., Seng, C. E., Lim, P. E., *Electronic J. of Environ., Agri. And Food Chem.*, 2007, **6**, 1764-1774.
21. Lagergren, S., *Handlingar*, 1898, **24**, 1-39.
22. Ho, Y. S., McKay, G., Wase, D., Foster, C. F., *Adsorp. Sci. Technol.*, 2000, **18**, 639-650.
23. Halaya, N. A., Kanamadi, R. D., Ramchandra, T. V., *Electronic J. of Biotechnology*, 2000, **8**, 341-350.
24. Hamadi, N. K., Chem, X. D., Farid, M. M., Lu, M. G. Q., *J. of Chemical Engineering*, 2001, **84**, 95-105.

25. Denizil, A., Ridvan, S., *J. of Biomaterial Science, Polymer Edition*, 2001, **12**, 1059-1073.
26. Gupta, V. K., Jain, C. K., Ali, I., Sharma, M., Saini, V. K., *Water Research*, 2003, **37**, 4038-4043.
27. Basyal, S. H., Din, G. O., *Applied Microbiol Biotechnol.*, 2004, **64**, 599-603.
28. Khan, N. A., Ibrahim, S., Subramaniam, P., *Malaysian J. of Science*, 2004, **23**, 43-51.
29. Sankararamakrishnan, N., Dixit, A., Iyengar, L., Sanghi, R., *Bioresource Technology*, 2006, **97**, 2377-2382.
30. Khan, N. A., Mohammad, H., *Water Research*, 2007, 37-41.
31. Ghimire, K. N., Inoue, K., Ohoto, K., Hayashida, T., *Sep. Sci. Technol.*, 2007, **42**, 2003-2018.
32. Ghimire, K. N., Inoue, K., Hayashida, T., *Biores. Technol.*, 2008, **99**, 32-37.
33. Bhattari, S. R., *An Unpublished M. Sc. Desertation*, 2009, T.U.
34. Raymundo, A. S., Zanarotto, R., Belisario, M., Godoi, M., Ribeiro, J. N., Riberio, A. V., *Braz. Arch. Biol. Technol.*, 2010, **53**, 931-938.
35. Humagai, P., Ghimire, K. N., Inoue, K., *Separation Sci. and Technology*, 2010, **46**, 818-824.
36. Lara, M. A. M., Rico, I. L. R., Vicenta, I. C. A., Garcia, G. B., deHoces, M. C., *Desalination*, 2010, **256**, 1-3.
37. Halim, A. A., Ezani, E., Othman, M. S., Awany, N., Ikram, M., *Australian J. of Basic and App. Sci.*, 2011, **5**, 1170-1177.
38. Mesifin, A. Y., Maitra, S., Eldemerdash, U., *J. of App. Sci.*, 2011, **8**, 1812-1854.
39. Karnitz, O. Jr., Grugel, L. V. A., deMelo, J. C. P., Botaro, V. B., Melo, T. M. S., Gil, R. P. F., Gil, L. F., *Bioresource Technology*, 2007, **98**, 1291-1297.
40. Sharma, D. C., Forster, C. F., *Bioresour Technol.*, 1994, **47**, 257-264.
41. Sharma, D. C., Forster, C. F., *Bioresour Technol.*, 1994, **49**, 31-40.
42. Esposito, A., Pagnanelli, F., Veglio, F. I., *Chem. Eng. Sci.*, 2002, **57**, 307-313.



**Table 1: Determination of calibration curve for Cr(VI)**

S.N.	i	ii	iii	iv	v	vi	vii	viii
Concentration (ppm)	0	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Absorbance	0	0.089	0.195	0.303	0.446	0.551	0.649	0.762

**Table 2: Determination of calibration curve for Al(III)**

S.N.	i	ii	iii	iv	v	vi	vii	viii
Concentration (ppm)	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Absorbance	0	0.111	0.189	0.258	0.386	0.483	0.571	0.664

**Table 3: Effect of pH on removal of Cr(VI) by RSCB**

pH <sub>i</sub>	pH <sub>e</sub>	C <sub>i</sub> (mg/L)	q <sub>e</sub> (mg/g)	% adsorption
1	1.21	24.53	8.43	34.36
2	2.42	24.68	7.66	30.82
3	3.51	23.89	4.37	18.29
4	4.23	24.76	3.64	14.7
5	5.34	24.41	2.25	9.2
6	6.11	24.42	1.07	4.42

**Table 4: Effect of pH on removal of Cr(VI) by MSCB**

pH <sub>i</sub>	pH <sub>e</sub>	C <sub>i</sub> (mg/L)	q <sub>e</sub> (mg/g)	% adsorption
1	1.5	23.81	22.42	94.51
2	2.34	24.52	20.07	85.97
3	3.51	24.67	13.54	54.88
4	4.29	24.45	10.67	43.64
5	5.61	23.91	6.39	26.72
6	6.34	24.58	2.72	11.06

**Table 5: Effect of pH on removal of Al(III) by RSCB**

pH <sub>i</sub>	pH <sub>e</sub>	C <sub>i</sub> (mg/L)	q <sub>e</sub> (mg/g)	% adsorption
1	1.21	24.34	1.11	4.56
2	2.46	24.67	2.3	9.32
3	3.51	23.83	3.21	13.47
4	4.29	24.72	5.34	21.6
5	5.34	24.51	7.96	32.48
6	6.33	24.29	8.87	36.51

**Table 6: Effect of pH on removal of Al(III) by MSCB**

pH <sub>i</sub>	pH <sub>e</sub>	C <sub>i</sub> (mg/L)	q <sub>e</sub> (mg/g)	% adsorption
1	1.34	24.72	2.59	10.47
2	2.51	24.35	9.67	39.71
3	3.21	23.77	14.55	61.21
4	4.47	24.48	17.23	70.38
5	5.23	24.39	20.34	83.47
6	6.22	24.21	21.49	88.76

**Table 7: Effect of concentration in the adsorption of Cr(VI) onto RSCB**  
**Volume of Cr(VI) solution: 25 ml**  
**Amount of adsorbent: 25 mg**  
**Optimum pH: 1.0**

concentration taken (mg/L)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$ (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (mg/L)
10	9.32	6.23	3.09	2.63	0.79	0.49
20	18.56	13.98	4.58	3.05	1.14	0.67
30	29.67	21.16	8.51	2.48	1.33	0.92
50	50.88	36.49	14.39	2.54	1.56	1.16
75	74.31	54.81	19.5	2.81	1.74	1.29
100	101.44	78.00	23.44	3.33	1.89	1.37
150	149.27	123.25	26.02	4.74	2.09	1.42
200	198.89	172.58	26.31	6.56	2.24	1.42
250	249.75	222.93	26.82	8.31	2.35	1.43
300	300.63	273.62	27.01	10.13	2.44	1.43
400	399.17	372.16	27.01	13.78	2.57	1.43

**Table 8: Effect of concentration in the adsorption of Cr(VI) onto MSCB**  
**Volume of Cr(VI) solution: 25 ml**  
**Amount of adsorbent: 25 mg**  
**Optimum pH: 1.0**

concentration taken (mg/L)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$ (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (mg/L)
10	10.32	2.40	7.92	0.30	0.38	0.89
20	19.27	4.58	14.69	0.31	0.66	1.16
30	31.06	4.67	26.40	0.18	0.67	1.43
50	48.72	8.29	40.43	0.21	0.97	1.59
75	74.39	15.15	59.24	0.26	1.37	1.70
100	100.91	29.55	71.36	0.41	1.57	1.80
150	151.11	58.98	92.13	0.64	1.79	1.95
200	198.46	87.74	110.72	0.79	1.98	2.00
250	249.55	123.14	126.42	0.97	2.12	2.07
300	299.82	169.39	130.43	1.29	2.25	2.09
350	349.63	218.42	131.21	2.00	2.44	2.09
400	401.45	269.77	131.68	2.04	2.43	2.11

**Table 9: Effect of concentration in the adsorption of Al(III) onto RSCB****Volume of Al(III) solution: 25 ml****Amount of adsorbent: 25 mg****Optimum pH: 6.0**

concentration taken (mg/L)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$ (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (mg/L)
10	9.20	5.07	4.13	1.23	0.705	0.62
20	18.46	9.11	9.35	0.97	0.96	0.97
30	31.24	17.70	13.54	1.32	1.25	1.13
50	50.89	30.13	20.76	1.45	1.48	1.32
75	73.27	48.93	24.34	2.01	1.69	1.39
100	98.56	72.129	26.43	2.73	1.86	1.42
150	151.15	123.11	28.04	4.39	2.09	1.45
200	198.07	167.93	30.14	5.57	2.23	1.48
250	249.57	216.022	33.55	6.44	2.33	1.53
300	298.88	264.822	34.06	7.78	2.42	1.53
400	399.01	315.40	34.24	9.21	2.49	1.53

**Table 10: Effect of concentration in the adsorption of Al(III) onto MSCB****Volume of Al(III) solution: 25 ml****Amount of adsorbent: 25 mg****Optimum pH: 6.0**

concentration taken (mg/L)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$ (g/L)	$\log C_e$ (mg/L)	$\log q_e$ (mg/L)
10	10.15	2.14	8.01	0.27	0.33	0.90
20	19.36	4.90	14.46	0.34	0.69	1.16
30	29.44	5.13	24.31	0.21	0.71	1.38
50	50.87	7.13	43.74	0.17	0.85	1.64
75	74.05	12.45	61.60	0.20	1.09	1.79
100	98.22	26.79	71.43	0.37	1.43	1.85
150	149.81	57.55	92.26	0.62	1.76	1.96
200	201.11	91.63	109.48	0.84	1.96	2.03
250	249.42	130.59	118.83	1.09	2.11	2.07
300	299.55	174.98	124.57	1.40	2.24	2.09
350	348.64	223.52	125.12	1.78	2.35	2.10
400	401.25	275.36	125.89	2.18	2.44	2.10

**Table 11: Kinetic data for the adsorption of Cr(VI) onto RSCB****Volume of Cr(VI) solution: 25 ml****Concentration of Cr(VI) solution: 25 ppm****Amount of adsorbent: 25 mg****Optimum pH: 1.0**

Time (minutes)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_t$ (mg/g)	$t/q_t$ (min.g/mg)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$1/(q_e - q_t)$
10	24.51	23.43	1.08	9.26	7.35	0.87	0.14
20	24.51	22.38	2.13	9.39	6.30	0.79	0.16
30	24.51	21.92	2.59	11.58	5.84	0.77	0.17
40	24.51	21.31	3.20	12.50	5.23	0.72	0.19
50	24.51	20.72	3.79	13.19	4.64	0.67	0.22
60	24.51	20.50	4.01	14.96	4.42	0.65	0.23
70	24.51	20.23	4.28	16.36	4.15	0.62	0.24
80	24.51	19.75	4.76	16.81	3.67	0.56	0.27
90	24.51	19.40	5.11	17.61	3.32	0.52	0.30
100	24.51	18.62	5.89	16.98	2.54	0.40	0.39
120	24.51	18.30	6.21	19.32	2.22	0.35	0.45
180	24.51	18.16	6.35	28.35	2.08	0.32	0.48
240	24.51	16.12	8.39	28.61	0.04	-1.39	25.00
300	24.51	16.09	8.42	35.63	0.01	-2.00	100.00
1440	24.51	16.09	8.43	170.82	-	-	-

**Table 12: Kinetic data for the adsorption of Cr(VI) onto MSCB****Volume of Cr(VI) solution: 25 ml****Concentration of Cr(VI) solution: 25 ppm****Amount of adsorbent: 25 mg****Optimum pH: 1.0**

Time (minutes)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_t$ (mg/g)	$t/q_t$ (min.g/mg)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$1/(q_e - q_t)$
10	24.63	20.52	4.11	2.43	16.01	1.20	0.062
20	24.63	19.57	5.06	3.95	15.06	1.17	0.066
30	24.63	18.51	6.12	4.90	14.00	1.47	0.071
40	24.63	16.53	8.10	4.94	12.02	1.08	0.083
50	24.63	15.47	9.16	5.45	10.96	1.04	0.091
60	24.63	14.98	9.65	6.22	10.47	1.02	0.095
70	24.63	14.05	10.57	6.62	9.55	0.98	0.105
80	24.63	13.42	11.21	7.14	8.91	0.95	0.112
90	24.63	13.02	11.61	7.75	8.51	0.93	0.118
100	24.63	12.27	12.36	8.09	7.76	0.89	0.129
120	24.63	11.57	13.05	9.19	7.08	0.85	0.141
180	24.63	5.46	19.17	9.39	0.95	-0.022	1.052
240	24.63	4.62	20.01	11.99	0.11	-0.96	9.091
300	24.63	-	20.12	14.91	-	-	-
1440	24.63	-	20.12	71.57	-	-	-

**Table 13: Kinetic data for the adsorption of Al(III) onto RSCB****Volume of Al(III) solution: 25 ml****Concentration of Al(III) solution: 25 ppm****Amount of adsorbent: 25 mg****Optimum pH: 6.0**

Time (minutes)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_t$ (mg/g)	$t/q_t$ (min.g/mg)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$1/(q_e - q_t)$
10	24.56	23.36	1.20	8.30	7.43	0.87	0.13
20	24.56	22.35	2.21	9.05	6.42	0.81	0.15
30	24.56	21.56	3.00	10.00	5.63	0.75	0.18
40	24.56	20.92	3.64	10.98	4.99	0.69	0.20
50	24.56	20.43	4.13	12.10	4.50	0.65	0.22
60	24.56	19.66	4.90	12.24	3.73	0.57	0.27
70	24.56	18.89	5.67	12.34	2.96	0.47	0.33
80	24.56	18.55	6.01	13.33	2.62	0.42	0.38
90	24.56	17.84	6.72	13.39	1.91	0.28	0.52
100	24.56	16.54	8.02	12.50	0.61	-0.22	1.64
120	24.56	16.24	8.32	14.42	0.31	-0.51	3.22
180	24.56	16.00	8.56	21.03	0.07	-1.16	14.28
240	24.56	15.93	8.63	27.81	-	-	-
300	24.56	15.93	8.63	34.76	-	-	-
1440	24.56	15.93	8.63	166.85	-	-	-



**Table 14: Kinetic data for the adsorption of Al(III) onto MSCB****Volume of Al(III) solution: 25 ml****Concentration of Al(III) solution: 25 ppm****Amount of adsorbent: 25 mg****Optimum pH: 6.0**

Time (minutes)	$C_i$ (mg/L)	$C_e$ (mg/L)	$q_t$ (mg/g)	$t/q_t$ (min.g/mg)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$1/(q_e - q_t)$
10	24.13	21.01	3.12	3.20	13.60	1.13	0.07
20	24.13	20.00	4.13	4.65	12.59	1.10	0.08
30	24.13	18.46	5.67	5.29	11.05	1.04	0.09
40	24.13	17.19	6.94	5.76	9.78	0.99	0.12
50	24.13	16.11	8.02	6.23	8.70	0.93	0.11
60	24.13	15.46	8.67	6.92	8.05	0.90	0.12
70	24.13	14.27	9.86	7.09	6.86	0.84	0.14
80	24.13	13.63	10.50	7.61	6.22	0.79	0.16
90	24.13	12.34	11.79	7.64	4.93	0.69	0.20
100	24.13	11.13	13.00	7.69	3.72	0.57	0.27
120	24.13	8.63	15.50	7.74	1.22	0.08	0.82
180	24.13	8.12	16.01	11.25	0.71	-0.15	1.41
240	24.13	7.76	16.37	14.66	0.35	-0.45	2.85
300	24.13	7.41	16.72	17.94	-	-	-
1440	24.13	7.41	16.72	86.12	-	-	-