

**ADSORPTION BEHAVIOUR OF CHROMIUM(VI) ONTO SURFACE
MODIFIED SUGARCANE WASTE**

**A Dissertation Submitted to the Central Department of Chemistry
Tribhuvan University, Kirtipur
Kathmandu, Nepal**

**In Partial Fulfillment of Requirements for the
Master's Degree in Chemistry**

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The dissertation entitled

**Adsorption Behaviour Of Chromium(VI) Onto Surface Modified
Sugarcane Waste**

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FOREWORD

The dissertation entitled “**Adsorption Behaviour Of Chromium(VI) Onto Surface Modified Sugarcane Waste** ” submitted by **Mr. Deepak Wagle** for the M. Sc. Degree in Chemistry has been carried out under my supervision in the academic year 2005-2007. During the research period (October 2007 to December 2008), he had performed his work sincerely & satisfactorily. No part of this thesis has been submitted for any other degree.

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At last but not the least, I would like to express my gratitude to my family for their co-operation and support throughout the entire period of the study.

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ABSTRACT

An effective chemically modified adsorbent based on sugarcane waste has been prepared by treating with concentrated sulphuric acid in 2:1 weight: volume ratio. Thus prepared adsorbent has been found to be effective in the adsorption of chromium from aqueous medium. The efficacy of the adsorbent in the removal of chromium was evaluated by batch adsorption method. The effect of initial concentration, contact time and pH of the solution was investigated. The maximum adsorption capacity onto this adsorbent was found to be 195 mg/g at their optimal pH 1 at which unmodified bagasse has only 58 mg/g. The characterization of adsorbent was done by determining surface area and Boehm's titration method. Freundlich isotherm and pseudo-second order kinetic model gave better explanation of the adsorption process.

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ABBREVIATIONS

L	=	Liter
g	=	Gram
mg	=	Milligram
mg/L	=	Milligram per liter
mL	=	Milliliter.
$\mu\text{g/L}$	=	Microgram per liter
%	=	Percentage
mg/g	=	Milligram per gram
mmol/kg	=	Millimol per kilogram
mol/kg	=	Mole per kilogram
ppm	=	Parts per million
%A	=	Percentage adsorption
pH _e	=	Equilibrium pH.
Cr(VI)	=	Hexavalent chromium.
DPCI	=	1, 5-Diphenylcarbazine.
q _m	=	Maximum adsorption capacity in mg/g
q _e	=	Amount adsorbed at equilibrium in mg/g.
q _t	=	Amount adsorbed at time 't' in mg/g.
C _e	=	Equilibrium concentration of metal ion in mg/L
C _i	=	Initial concentration of metal ion in mg/L
C _t	=	Concentration of metal ion at time 't' in mg/L
V	=	Volume of metal solution in Liter
W	=	Weight of adsorbent used in gram
1/n	=	Adsorption intensity
K	=	Adsorption capacity
K _L	=	Langmuir equilibrium parameter
b	=	Langmuir constant in L/mg

K_1	=	Pseudo first order rate constant in min^{-1}
K_2	=	Pseudo second order rate constant in g/mg.min
K_2^1	=	Second order rate constant in g/mg.min
V_0	=	Initial adsorption rate in mg/g.min .
ε	=	Molar Excitation coefficient

1. Introduction

1.1 General Introduction

Heavy metals are toxic pollutants released into aquatic ecosystem as a result of different human activities such as industrial, mining and agricultural activities. This includes electroplating, leather tanning, cement, mining, dyeing, fertilizer and photography industries.¹ These heavy metals includes as Cr(VI), Cd(II), Pb(II), Fe(III), Ni(II), Zn(II) Cu(II) etc.² These heavy metals are non biodegradable and intake at appreciable amount may cause health problem to animal, plants, human being and environmental problem as well.

Hexavalent chromium has been reported to be toxic to animals and humans and known to be carcinogenic.¹ In addition, it leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation.³ The tolerance limit for Cr(VI) for discharge into inland surface waters is 0.1 mgL^{-1} and in potable water is 0.05 mgL^{-1} . But its concentration in industrial waste water ranges from $0.5\text{-}270 \text{ mgL}^{-1}$. In order to comply with environmental regulatory limit, it is essential that these effluents must be treated and Chromium(VI) concentration should be made reduced to acceptable limit.¹

There are different methods of treatment of Cr(VI) contaminated water. They are chemical precipitation, lime coagulation, ion-exchange, reverse osmosis, solvent extraction, reduction, electrodialysis, evaporation, electrochemical precipitation etc.^{1, 2, 4, 5} However these methods are not widely acceptable due to high capital and operational costs and problem in disposal of residual metal sludge. Biosorption is an effective and versatile method for removing Cr(VI) and other heavy metals from heavy metal contaminated effluents. There are number of biosorbents which have been investigated for the removal of different metal from aqueous solution.⁶

The surface modified carbon is commonly used as an adsorbent for the removing of Cr(VI) because of its effective adsorption capacity in trace level at low cost. Modified carbon has been prepared from the various agriculture waste as sugarcane bagasses, rice husk, coconut shell, Banana bark, pine leaf, wood and dust, Lapsi seeds etc.¹ These carbon which are prepared from agriculture waste contain high percentage of carbon and have fairly high adsorption capacity for heavy metals including Cr(VI). A great interest has been focused to understand the mechanism of adsorption of Cr(VI) in carbon prepared from agriculture waste.¹ The carbon prepared from agriculture waste can be activated by various method like chemical modification, steam activation, thermal activation etc. By means of such activation, the effective surface area of carbon increases and surface of the adsorbent gets modified due to formation of different functional groups.⁷

In Nepal lots of biomaterial like, sugarcane bagasses, rice husk, maize barn, apple waste, orange waste and banana bark are easily available as waste material. Sugarcane is one of the very popular in making sugar and the waste thus produced is abundantly found in Terai region of Nepal. Similarly juice vending centers in different location of Kathmandu valley produce huge amount of sugarcane bagasses. Every year tons of sugarcane bagasses are generated as waste material, it is burnt as a less efficient fuel causing air pollution mainly during harvesting season. Therefore it is quite suitable to use as an adsorbent rather than wasting.

In present research work, sugarcane bagasses collected from juice vending center of kathmandu has been explored to convert into cost effective environmental friendly bioadsorbent for the removal of Cr(VI) from aqueous solution. Hexavalent chromium, Cr(VI) exist in the aqueous solution as oxy anions such as chromate(CrO_4^{2-}), dichromate($\text{Cr}_2\text{O}_7^{2-}$), (HCrO_4^-) and (HCr_2O_7^-) form.²

1.2 Experimental

The phenomenon of increasing the concentration of substance on the surface of a solid or liquid than in the bulk of solid or liquid is called adsorption. The substance onto which adsorption takes place is called as adsorbent and which get adsorb is called as adsorbate. The adsorption of various metals onto adsorbent can be studied by Column and Batch experiment.

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 of the column using a flow controller. Effluent samples were collected at each interval of time and examine for residual metal content to evaluate the efficiency of the column. The metal concentration before and after adsorption is measured by using spectrophotometer.

In batch experiments, a definite mass of the adsorbent is agitated with the predetermined volume of metal solution into the stopper bottle. Stoppered bottle is vigorously shaken in a mechanical shaker at room temperature for 24h to attain adsorption equilibrium. The initial and equilibrium concentrations of metal ions are determined using spectrophotometers. ^(1, 4, 8, 9)

Heavy metal adsorption onto adsorbent is affected by different parameters such as initial concentration of metal ions (mg/L, contact time (in minutes), amount of adsorbent used (g/L), temperature (°C) and pH of the solution. ^(4,10) To understand the mechanism and effectiveness of adsorption, any one of the above parameter is varied by keeping the other parameters constant. ⁴

From the metal concentration measurement before and after adsorption, amount of metal ion adsorption onto adsorbent is determined by using following relation as¹.

$$\therefore q_t = \frac{C_i - C_e}{W} \times V \dots\dots\dots (I)$$

Where, C_i and C_e are initial & equilibrium metal ion concentration in mg/L respectively. q_t is the amount of metal adsorbed at time 't' in mg/g.

V is the volume of metal solution in L.

W is the weight of adsorbent in gm.

Metal removal percentage is calculated by using a formulate

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

This is the ratio of decrease in metal ion concentration before and after adsorption to the initial concentration.

1.3 Preparation of Adsorbent

Biosorbent are the biomass material which have different adsorption capacities. The adsorption capacity of such adsorbent can be increased by different methods as thermal activation, chemical modification & so on. Sugarcane bagasses consist of cellulose, hemicelluloses, lignin, polyphenol and many other low molecular weight compounds.⁸ Sugarcane bagasses were collected from juice vending centers. It was washed with distilled water and dried in sunlight and finally dried in oven at 100°C for 3h. It was cut into small pieces and grounded to powder and sieved to pass through 250 μm. Chemical modification using concentrated H₂SO₄ at moderate temperature is supposed to activate polyphenolic/polyhydroxy surface functional groups contained in sugarcane waste. The material was mixed in a 2:1 weight: volume ratio of concentrated H₂SO₄ and allowed to soak for 24h at room temperature. The samples were then washed with distilled water till pH of the modified carbon becomes neutral and dried at 80°C for 5h.

Modification mechanism of adsorbent ¹¹

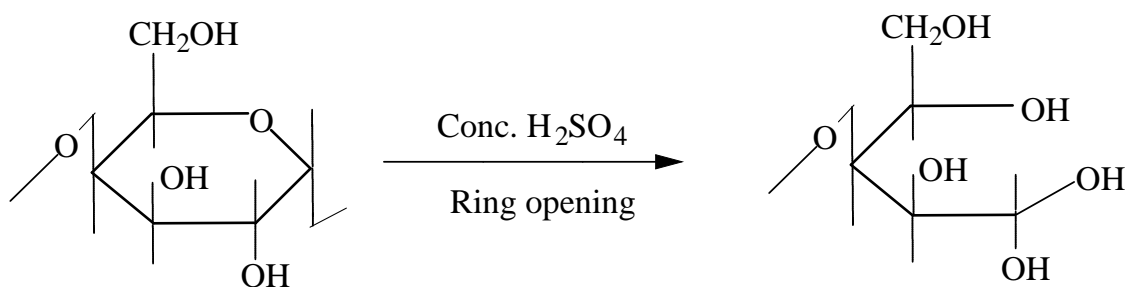


Fig: 1. Schematic representation for the ring opening of monomeric unit of cellulose contained in sugarcane waste by the treatment with concentrated H₂SO₄.

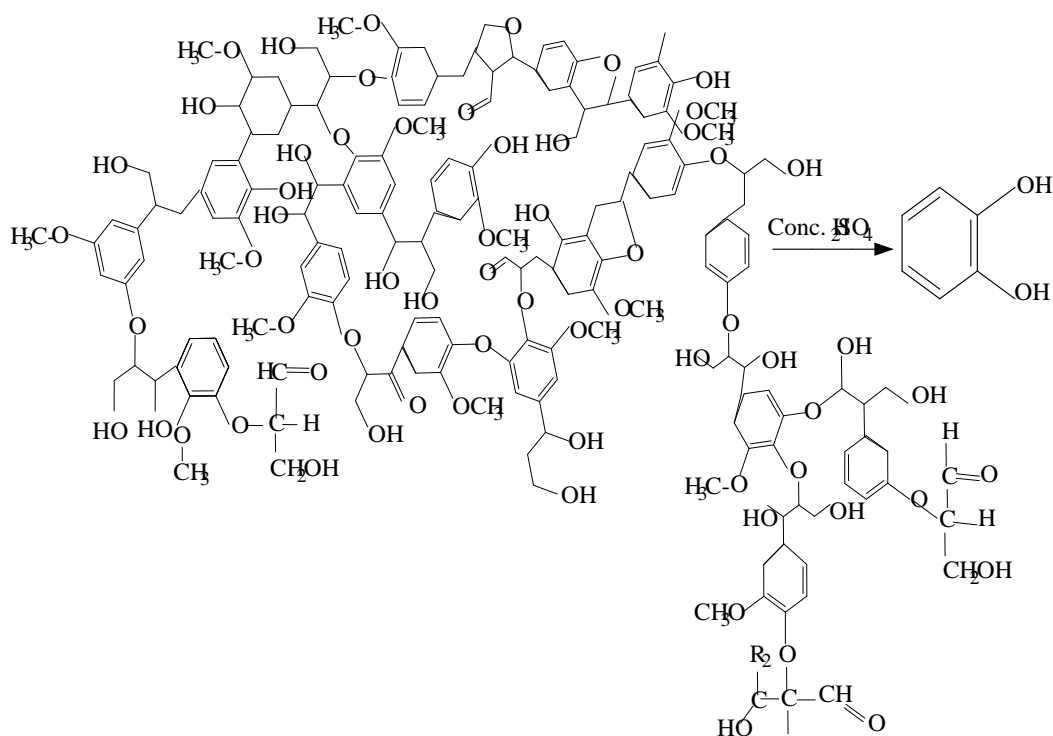


Fig:2 Systematic representation for the isolation of polyphenolic group from lignin contained in sugarcane waste by the treatment with concentrated H₂SO₄.

1.4 Characterization of Adsorbent

1.4.1 Determination of Surface Area

The extent of adsorption highly depends on the surface functional groups of the adsorbent. Higher the available surface functional groups 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 adsorption.¹² However in our case surface area was determined by the formula.¹³

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

Where,

N = Avogadro's number (6.023×10^{23}).

S = Specific surface area

b = Langmuir constant

1.4.2 Titration studies (Boehm's titration)

According to H.P. Boehm's only strong acidic carboxylic acids groups are neutralized by sodium bicarbonate, where as these neutralized by sodium carbonate is thought to be lactones, lactol and carboxylic groups. The weakly acidic phenolic groups only react with strong alkali sodium hydroxide. Therefore, by selective neutralization using bases of different kinds, the surface acidic functional group in carbon can be characterized both quantitatively and qualitatively. Neutralization with hydrochloric acid characterizes the amount of surface basic groups that are for example pyrones and chromens. This indicates that chemically modified sugarcane waste materials may possess acidic oxygen functional group on their surface. The basic properties have described to surface basic groups and the pi electron system of carbon basal planes.^(4,7)

A method based on Boehm's was modified to a certain total titrable surface functional groups to quantify the amount of various types of polyphenolic/ polyhydroxy groups contained in sugarcane waste. The volume of NaOH required to neutralize the sample was converted to total titrable surface functional groups.⁷

1.5 Adsorption Isotherm

Adsorption isotherm is a curve which relates the amount of the adsorbed per unit mass of adsorbent to the amount of unadsorbed adsorbate remaining in the solution at equilibrium time. Experimentally isotherms are useful for describing adsorption capacity to evaluate the feasibility of these processes for a given application.¹⁴ The Langmuir and Freundlich isotherms are most frequently used to represent the data of sorption from aqueous solution. Langmuir adsorption isotherm is given by.¹⁵

$$\frac{C_e}{X} = a + bC_e \dots\dots\dots (IV)$$

Where, C_e is the concentration of adsorbate, which is in dynamic equilibrium with the adsorbents adsorbed on charcoal, x is the amount of adsorbate adsorbed per gram charcoal, and 'a' and 'b' are Langmuir constant.

Langmuir adsorption isotherm can be rearranged and the linear form of Langmuir equation is given by.^(2, 14, 16)

$$q_e = \frac{q_{max} \times bC_e}{1 + bC_e} \dots\dots\dots (V)$$

This equation can be further simplified as,

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

Where q_e is milligram of metal accumulated per gram of the adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), q_m the maximum adsorption capacity and b is the Langmuir adsorption equilibrium constant (L/mg). When C_e/q_e is plotted against C_e , then a straight line with a slope equal to $1/q_m$ and intercept $\frac{1}{q_m b}$ obtained from which q_m value can be calculated.

According to Hay *et.al* (1996), the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (K_L) which is defined by the following relationship.^(2,17)

$$K_L = \frac{1}{1 + bC_i} \dots\dots\dots (VII)$$

Where C_i is the initial concentration of the adsorbate (mg/L) and K_L is the Langmuir equilibrium parameters. The parameters K_L indicate the shape of isotherm and nature of the adsorption process. ($K_L > 1$ for unfavorable, $K_L = 1$ favorable, $K_L = 0$ for irreversible^(2, 16) the K_L values lies between 0.8475 to 0.15625 for concentration of 200-600 mg/L of Cr(VI) solution.²

The Linear form of Freundlich model is represented by the following equation.¹⁴

$$q_e = KC_e^{1/n} \dots\dots\dots (VIII)$$

In logarithmic form

$$\log q_e = \log k + 1/n \log C_e \dots\dots\dots (IX)$$

Where, 'K' and 'n' are the Freundlich constant which are considered to be the relative indicators of adsorption capacity and adsorption intensity. The

value of $1/n$ varies between 0-1 indicates the favorable adsorption of heavy metal.¹⁸

1.6 Adsorption Kinetics

Adsorption kinetics study is the study of rate and mechanism of the adsorption process. There are numerous adsorption kinetics models that are used to describe the uptake of adsorbate by different adsorbent. The pseudo-first order rate equation (Lagergren, 1898), the pseudo second order rate equation (Ho *et.al.* 2000) and second order rate equation (Ho *et.al.* 1996) has been used widely for the description of adsorption kinetic model. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (R^1 values close or equal to 1). A relatively higher value indicates that the model successfully describe the kinetic of adsorption.^(1, 19)

1.6.1 The pseudo First order model

The linearised form of pseudo first order model is generally expressed as follows.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots\dots\dots (X)$$

Where q_e and q_t are amount of metal adsorbed at equilibrium and at time t , respectively (mg/g). K_1 is the rate constant of pseudo first order adsorption ($L \text{ min}^{-1}$).^(1, 20)

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (X) becomes

$$\text{Log}(q_e - q_t) = \text{log}(q_e) - \frac{K_1}{2.303} t \dots\dots\dots (XI)$$

The plot of $\log (q_e - q_t)$ vs 't' should give a straight line from which k_1 and q_e can be determined from slopes and intercept of the plot respectively.

1.6.2 Pseudo-second Order Model

The pseudo second order adsorption Kinetic rates equation is expressed as (Ho *et. al.* 2000) ^(1, 20)

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

Where K_2 is the pseudo second order rate constant $mg^{-1} min^{-1}$ and q_e and q_t are the amount of metal ion adsorbed at equilibrium and at time 't' respectively (mg/g).

By applying boundary condition $t = 0$ to $t = t$ & $q_t = 0$ to $q_t = q_t$ the integrated form of equation (XII) becomes.

$$\left(\frac{t}{q_t} \right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} (t) \dots\dots\dots (XIII)$$

If initial adsorption rate v_o $mgg^{-1} min^{-1}$ is

$$v_o = K_2 q_e^2 \dots\dots\dots (XIV)$$

Then equation (xiii) becomes

$$\left(\frac{t}{q_t} \right) = \frac{1}{v_o} + \frac{1}{q_e} (t) \dots\dots\dots (XV)$$

The plot of t/q_t vs t of equation (XIII) should give a straight line having slope $1/q_e$ and intercept $\frac{1}{K_2 q_e^2}$. So the pseudo second order rate constant and amount of metal ion adsorbed at equilibrium can be calculated. ¹

1.6.3 The Second order model

The second order adsorption kinetic rate equation is expressed as (Ho *et. al.* 1996).

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_3} + k_2^1(t) \dots\dots\dots (XVI)$$

Where, q_e and q_t have their respective meaning. 't' is contact time and K_2^{-1} is second order rate constant (g/mg. min). The plot of $(1/q_e - q_t)$ vs 't' should be a straight line with slope equal to K_2^{-1} & intercept $1/q_e$.¹⁹

1.7 Spectrophotometric Method

A more sensitive method for the determination of Chromium(VI) is diphenyl carbazide indicator (DPCI) method, in which Cr(VI) form a pink colored complexes with 1,5- diphenylcarbazide in acidic medium and can be spectrophotometrically analyzed.^(1, 21, 22,23)

2. Literature Survey

There are different methods of the treatment of Cr(VI) contaminated water like chemical precipitation, lime coagulation, ion exchange, reduction, reverse osmosis, solvent extraction, electro dialysis, electrochemical precipitation, cementation etc.^(1, 2, 4, 5) However these methods are not widely acceptable due to high operational costs and problem in disposal of residual metal sludge. Owing to this reason much attention has been given to investigate the cheaper technique. Recently, biological waste material for the heavy metal removal has been increasing because of their high metal binding capacity and cost effective nature.

Adsorption process has been found to be one of the alternatives to lower down the concentration of Chromium from aqueous solution. This can be removed by adsorption onto various adsorbents derived from different sources. One of the most widely used adsorbent is charcoal which can easily removed Cr(VI) from aqueous solution. Charcoal can be prepared from various sources like sawdust, rice husk, rubber wood, fruit shell, fruit seed etc. However, activated charcoal seems to be less effective as compare to that of functionalized materials derived from several sources.

Dodrowolski *et.al*²⁴ studied the adsorptions of Cr(VI) from aqueous solution on activated carbon and found that the reaction rate of ions on the surface of the activated carbon rather than diffusion was the major process influencing the equilibrium. Surface reduction of Cr (VI) to Cr (III) appeared to be the principal mechanism for the adsorption of chromium on the activated carbon.

Arivoli *et.al*.⁴ studied the adsorption of chromium ion from aqueous solution by acid activated banana bark carbon and show have effect of variable parameter on adsorption process and maximum adsorption takes

place at low and high pH value and the amount of adsorption increased with increasing ionic strength and temperature. They calculate the different thermodynamic parameters as ΔH° , ΔS° , ΔG° .

Nomanbhay *et.al.*³ studied removal of heavy metal from industrial waste using chitosan coated oil palm shell charcoal and they found that chromium ion removal by using this adsorbent was appeared to be technically feasible eco-friendly and with high efficiency. Besides that the adsorbent can be regenerated by using sodium hydroxide and therefore can be reused.

Hamadi *et.al.*²⁵ studied the adsorption kinetics for the removal of Cr(VI) from aqueous solution by tyres & Sawdust. They found that the removal was favored at low pH, with maximum removal at pH 2. They found both sorbet were effective to remove Cr(VI) from solution. The sorption kinetics was found to follow pseudo second-ordered model.

Ahalya *et.al.*² studied biosorption of Cr(VI) from aqueous solution by the husk of Bengal gram. They found that the removal was favored at pH 2. The adsorption data fit well with the Langmuir & Freundlich isotherm model. The biosorption of Cr(VI) was possible due to the ion exchange with hydrogen of OH & -COOH groups presents in the lignocelluloses moieties.

Demirabas *et.al.*¹ studied the adsorption kinetics for the removal of Cr(VI) from aqueous solution on the activated carbon prepared from cornelian cherry, apricot stone and almond shells. They found that the maximum adsorption of Cr(VI) at pH 1 for all types of carbons. The sorption reaction was found to be follow pseudo second order model.

Baral *et.al.*²⁰ studied the Hexavalent chromium removal from aqueous solution by adsorption on sawdust. The studies were conducted by varying various parameters such as contact time, pH, amount of adsorbent,

concentration of adsorbate & temperature. They found that the maximum removal of Cr(VI) in the pH range 4.5-6.5 & sorption reaction was found to be follow pseudo-second order.

Sankararamakrishnan and Sanghi ¹⁹ studied the adsorption of Cr (VI) on novel xanthated chitosan. They found that the maximum uptake of Cr(VI) by chemically modified chitosan at pH 3. Such chemically modified xanthated chitosan might find potential use as adsorbent in tannery wastewater treatment.

Khan and Mohamad ⁵ studied investigations on the removal of Cr(VI) by sugarcane bagasse from wastewater. The effect of various parameters on the removal process and found that removal was effective at low pH 1 and contact time 4 h. The adsorption data obtained during the studied well fitted with the Freunlich isotherm.

Gupta and Babu ²⁶ studied the adsorption of Cr(VI) by low cost adsorbent prepared from amarind seeds. They found that the adsorbent prepared from amarind seeds can be used for removal of Cr (VI) from aqueous solution and adsorption was favorable at low pH. Freundlich adsorption model showed good agreement with the experimental data.

Nameni *et.al.*²⁷ studied adsorption of hexavalent chromium from aqueous solution by wheat bran. They studied the effect of various parameters on Cr(VI) adsorption and found that the adsorption of chromium by wheat barn reached to equilibrium after 60 minutes and maximum chromium removal (87.8%) obtained at pH 2. The result showed that the adsorption follow the pseudo second order kinetics.

Though there are several works regarding the adsorption onto either using activated carbon or with biomaterials as such. Now a day, the great attention has been paid to remove the heavy metals by using functionalized

biopolymers. Under such circumstances, this dissertation has explored a possibility to derive polyphenolic/ polyhydroxy functional matrix in sugarcane waste for the purpose of chromium adsorption.

3. Objective of the Present Study

The objectives of this entire research work are to investigate adsorbent with suitable functional groups for the binding of Chromium by making simple chemical modification of the sugarcane waste. In principle, the target of this research was to create the polyphenolic/ polyhydroxy functional groups as much as possible onto the polymer matrix of sugarcane waste.

3.1 General Objective

The general objective of the present work was to prepare low cost bio-adsorbent from the agricultural waste as for examples sugarcane bagasse and to investigate the adsorption capacity of the adsorbent in the removal of Cr(VI).

3.2 Specific Objective

The specific objectives of the present works are

- ❖ To prepare and characterize the adsorbent for absorption of Cr(VI) from aqueous solution.
- ❖ To find out the nature of adsorption isotherm in the removal of Cr(VI) from aqueous solution.
- ❖ To investigate the effect of pH, initial concentration of absorbate and contact time in the removal of Cr(VI) from aqueous solution.
- ❖ To study the kinetics of the adsorption reaction and to find out the nature of adsorption isotherm in the removal of Cr(VI) from aqueous solution
- ❖ To compare the adsorption capacity of chemically modified sugarcane bagasses with unmodified sugarcane bagasses as adsorbent.

4. Methodology

4.1. Preparation of the Reagents

4.1.1 Potassium Dichromate ($K_2Cr_2O_7$) Stock Solution (1000 ppm)

Stock potassium dichromate solution was prepared by dissolving 2.514 gm of potassium dichromate crystal in 1000 mL volumetric flask in 0.1 M HNO_3 solutions¹⁵.

1mL of stock potassium dichromate solution=1000 μg $HCrO_4^-$ as in the form of Cr(VI).

From stock potassium dichromate solution, working solution of lower concentration was prepared by dilution method in 0.1N nitric acid. By dilution method solution of 10 mg/L, 20 mg/L, 30 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 250 mg/L, 300 mg/L, 350 mg/L, 400 mg/L, 450 mg/L, 500 mg/L was prepared in volumetric flask (250mL) by using 0.1 M HNO_3 solution.

4.1.2 5M Sulphuric Acid Solution (approx)

5M of Sulphuric acid solution was prepared by diluting 34.7mL of concentration sulphuric acid in 250 mL volumetric flask in distilled water.

4.1.3 5M Sodium Hydroxide Solution (approx)

5M sodium hydroxide solution was prepared by dissolving 20 gm of sodium hydroxide pellets in 100 mL volumetric flask in distilled water.

4.1.4 5 M Nitric Acid Solution (approx)

5M nitric acid was prepared by diluting the 32 mL of concentration. HNO_3 (15.66M) in 100 mL volumetric flask in distilled water.

4.1.5 Preparation of 0.25% 1,5 Diphenylcarbazide (DPCI) Solution

0.25 gm of 1,5-diphenylcarbazide crystals were transferred to a 100mL volumetric flask and 50mL of pure acetone was added slowly with constant striking. Then 50mL water was added up to the mark. Due to the high sensitivity of this solution to light, it was protected from direct sunlight by wrapping the bottle containing the reagent with black paper. This prolonged the life span of the reagent. When this solution turned faint red, it was discarded and a fresh solution was prepared.

4.1.6 Buffer Solution pH 4

Buffer tablet of pH 4 was dissolved in a 100 mL volumetric flask and made up to the mark in distilled water.

4.1.7 Buffer Solution of pH 7

Buffer tablet of pH 7 was dissolved in 100 mL volumetric flask and made up to the mark in distilled water.

4.1.8 Buffer Solution of pH 9.2

Buffer tablet of pH 9.2 was dissolved in a 100 mL volumetric flask and made up to the mark in distilled water.

4.2 Analysis of Chromium

Chromium(VI) solution of 20 mg/L of volumes 0, 1, 2, 3, 4, 5, 6, 7, 8 and 9 mL were taken in a different 25mL volumetric flask and was acidified with 1 mL of 5 M H_2SO_4 solution. Then 1mL of 0.25% DPCI solution was added to each volumetric flask and shaken well for 15 minutes. The volume was made up to the mark by adding water.²³

The absorption spectra of pink colored Chromium(VI) diphenylcarbazide complex was recorded by using sytonic spectrophotometer-103 against blank solution. At λ_{max} the absorbance of all the solution were measured against reagent black using same spectrophotometer and calibration curve was drawn. The absorbance spectra and calibration curve i.e. Lambert-Beer plots are given in Fig 4 and 5.

4.3 Batch Adsorption Studies

Batch adsorption studies were carried out with unmodified sugarcane bagasses and modified charcoal and investigated the effect of initial concentration of metals, pH of the solution and contact time of the adsorption process. Most of the chemical used were of LR grade. Solution of various concentration of metal ion ranged from 20 mg/L to 500 mg/L were prepared by diluting the 1000 mg/L stock solution in a series of way.

The pH of the solution was adjusted by using the HNO_3 solution having concentration 1 M to 5 M or NaOH solution having same series of concentration. 25mL of the metal solution with known concentration was taken in 125mL reagent bottle and added predetermined amount of adsorbent. It was equilibrated in a mechanical shaker for 24h at room temperature. Then the solution was filtered using filter paper and filtrate solution was analyzed for the remaining concentration of metal ion using spectrophotometer. The

concentration before and after adsorption were determined by sytonic spectrophotometer-103.

4.3.1 Batch pH Studies

Batch pH studies were conducted by shaking 25 mL of metal solution containing 20 mg/L metal with 25 mg of adsorbent (modified & unmodified) for 24h with initial pH values 1, 2, 3, 4, 5 and 6 respectively. The pH of the solution was measured by using WPA CD 300 digital pH meter. Each sample solution was shaken in 125mL reagent bottle by using mechanical shaker at room temperature. Then the solution was filtered and equilibrium pH of the solution was measured. The concentration of the solution before and after adsorption was determined with the help of spectrophotometer. In this process the solution was diluted up to the detection limit range of spectrophotometer. The pH value of at which maximum adsorption of metal occurs was selected as optimum pH for the further studies.

4.3.2 Batch Equilibrium Time Studies

Equilibrium time for the adsorption of Cr(VI) onto modified and unmodified sugarcane bagasses were studied at optimum pH value at room temperature. 25mL solution of known concentration was taken in 125mL reagent bottle with predetermined amount of adsorbent and was equilibrated in a mechanical shaker for, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 min, 20 h, 21 h, 22 h& 24 h. Residual concentration of the solution before and after adsorption were analyzed by Sytonic Spectrophotometer-103.

4.3.3 Batch Isotherm Studies

Batch isotherm studies were carried out with different initial concentration at optimum pH of metal ion ranging from 20 mg/L to 500 mg/L of metal ion with 25 mg of adsorbent were equilibrated in mechanical shaker

for 24h and metal concentration before and after adsorption were analyzed by using Systonic Spectrophotometer-103.

4.3.4 Batch Kinetics Studies

Batch kinetic studies were carried out by shaking 25 mg of adsorbent with 25 mL of 20 mg/L of metal solution in 125 mL reagent bottle. The kinetics was investigated by drawing sample after the desired contact time and filtrate was analyzed for the remaining metal ion concentration. The concentration of the metal solution before and after adsorption was determined by using spectrophotometer. The data obtained were analyzed with pseudo-first order (Lagergren, 1898) Pseudo-second order (Ho and Ackaya *et.al.*(2000) and second order (lagergren, 1998) model.

5. Result and Discussions

5.1 Absorbance Spectra and Calibration Curve for Cr(VI) complex with DPCI.

Figure 4 represents the absorption spectra of the pink-colored complex of Cr(VI) - diphenylcarbazide complex in 5 M H₂SO₄ solution. The nature of spectra and λ_{max} at 540 nm matched with the reported value. ^(1, 2, 22)

Figure 5 represents the Lambert - Beer's plot for Chromium(VI)-diphenylcarbazide complex at 540 nm. A linear relation was found between the absorbance of Cr(VI) diphenylcarbazide complex and the concentration of chromium.

5.2 Characterization of Charcoal

5.2.1 Surface Area Determination

The surface area of the sugarcane bagasses waste was determined by acetic acid adsorption techniques. The surface area of the modified sugarcane waste was found to be 113.10 m²/g.

5.2.2 Titrimetric method (Boehm's Titration)

The amount of total titrable surface functional group of sugarcane waste was evaluated by Boehm titration & which was found to be 3.2 mol/kg that is, 372.67 mg/g. Thus, it can be concluded that surface functionalized sugarcane waste bearing polyphenolic/ polyhydroxy functional groups can be used for the sorption of chromium from the synthetic aqueous solution.

5.3 Effect of pH Studies

Figure 6 shows the effect of pH in the adsorption of Cr(VI) onto modified sugarcane waste and unmodified sugarcane waste at an initial concentration of 20 ppm at laboratory temperature. The amount of adsorption decreases from 18.375 (98%) to 5 (26.66%) in case of surface modified waste and 13.75 (61.79%) to 1.16 (0.94%) to unmodified material when the pH of the solution increased from 1 to 6. This indicates that the adsorption of chromium is clearly dependent on pH. It is obvious that pH determines the extent of the Cr(VI) removal as well as providing a favorable removal adsorbent surface charge for the adsorption to occur. At low pH, chromium exists as HCrO_4^- . The reason of maximum adsorption at low pH is due to the favourable complexation of the chromium with polyphenolic/ polyhydroxy functional groups of the modified sugarcane waste. From the batch pH studies it was found that the adsorption of Cr(VI) are found to be effective at pH 1.

5.4 Effect of Initial Concentration

Figure 8 shows the removal of chromium(VI) by adsorption onto unmodified sugarcane waste and surface modified sugarcane waste. The adsorption increases at lower concentration range to higher concentration range and attained an equilibrium value. On changing the initial concentration of Cr(VI) from 20 mg/L to 450mg/L, the amount adsorbed increased from 18.375 mg/g to 195 mg/g in case of surface modified material & 13.75 mg/gm to 58 mg/g in case of unmodified material at pH 1. This result concluded that when the material is modified, the amount adsorbed had increased by 70%.

5.5 Effect of Contact time

Figure 9 shows the adsorption of Cr(VI) onto unmodified waste and surface modified waste from 10 minutes to 24 h. Adsorption of chromium onto these material is found to be constant after 250 min and 90 minutes, respectively. The metal adsorption capacity is high at initial time because of the presence of large number of complexation sites. The sorption capacity decreases with time due to decrease in active sites in the adsorbent and after saturation sorption becomes constant.

5.6 Batch Isotherm Studies

Adsorption of Cr(VI) onto surface modified and unmodified material gives the linear relationship with Langmuir and Freundlich isotherm. This is shown in Figure 10 and 11. Langmuir and Freundlich parameters are determined from the slope and intercept of their respective plots. Their values are tabulated in Table 9. From Table 10, the value of Langmuir equilibrium parameter lies between 0 and 1 indicating that equilibrium data fits well with Langmuir adsorption isotherm.

On the other hand, Freundlich adsorption isotherm of surface modified and unmodified material indicated that the equilibrium data fits well with Freundlich adsorption isotherm. The value of $1/n$ lies between 0-1 indicating favorable adsorption.

However, the correlation coefficient value for Freundlich isotherm is found to be greater than that of Langmuir plot. So the adsorption process revealed to follow Freundlich isotherm.

5.7 Batch Kinetic Studies

Kinetic studies for the adsorption of Cr(VI) onto chemically modified sugarcane waste and unmodified waste were studied using pseudo-first order (Lagergren, 1989) pseudo-second order (Ho, *et. al.* 1995 and Ho and Mckay *et. al.* 2000) and second order (Lagergren, 1898) model. It was observed experimentally from the present studies that the adsorption kinetics behavior of Cr(VI) onto these adsorbent was found to follow only pseudo-second order kinetic model but not pseudo-first order model and second order model.

For 1st order model the plot of $\log(q_e - q_t)$ versus 't' should be a straight line with -ve slope value but when we plot this values we get a line with +ve slope value. Similarly for second order when we plot a graph between $\frac{1}{q_e - q_t}$ versus 't' we should not get a straight line with +ve value of slope. So we concluded that the adsorption process does not follow pseudo 1st order model and second order model.

But when we plot a graph for $\frac{t}{q_t}$ versus 't' we get a straight line with slope having +ve value (0.077) according to pseudo second order model. So adsorption studies of Cr(VI) on surface modified waste follow pseudo-second order kinetic model. This is represented in Figure 12.

6. Plausible Adsorption Mechanism

Based on the distribution diagram, the adsorbed chemical species of the chromium was revealed to be HCrO_4^- at optimal pH 1. Since the chemically modified sugarcane waste possesses higher amount of polyphenolic/ polyhydroxyl functional group as discussed in earlier section, a plausible mechanism of chromium(VI) adsorption can be schematically represented as follows:

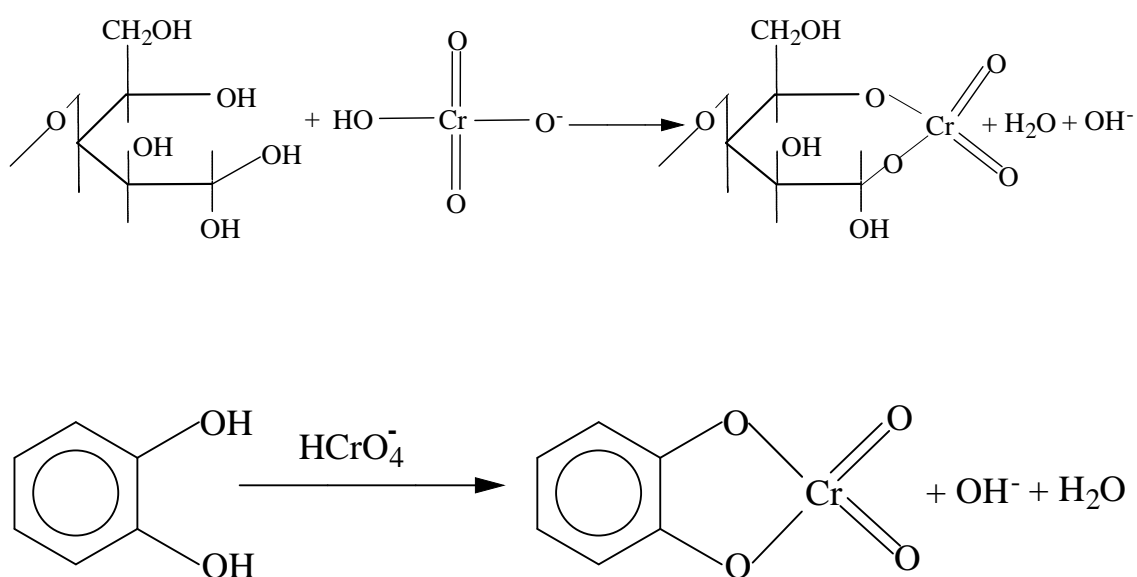


Fig: 3. Complexation of Chromium(VI) with polyphenolic/polyhydroxyl functional moiety of modified sugarcane waste

7. Conclusion

An effective adsorbent for the removal of the chromium has been investigated by making simple chemical modification of the sugarcane waste. The maximum chromium uptake capacity of the adsorbent prepared at our laboratory was found to be as superior as compared to the researches made by the other several researchers. Thus it can be concluded that chemically modified sugarcane waste can be used in the separation /purification of chromium from waste water.

The maximum adsorption capacity of Cr(VI) onto chemically modified sugarcane waste was found to be 195 mg/g and that for unmodified bagasses 58 mg/g at their optimal pH 1.

The required equilibrium time for the adsorption of Cr(VI) onto chemically modified sugarcane waste was 90 min whereas for unmodified material was 250 minutes, respectively. The pseudo-first order, pseudo second order and second order model were used to analyses the kinetic data and it was found the pseudo-second order model gave better description to experimental data.

Characterization of adsorbent was done by evaluating surface area and total surface functional groups of modified material. The total titrable surface functional group was found to be 3.2 mol/kg which is equivalent to 372.67 mg of chromium per gram of the chemically modified sugarcane waste. Surface area of the chemically modified waste was found to be 113.10 m²/g

8. Application of the Research Work:

Surface modified sugarcane waste is one of the cost effective adsorbent which can be employed for adsorptive removal of the Chromium(VI) from industrial waste water.

Since, surface modified sugarcane waste adsorbed mainly anionic species, it can be employed for the removal of phosphate (PO_4^{3-}), nitrate (NO_3^-) etc.

9. Limitation of the Study

The limitation of the present study were

- ❖ Adsorption process was studied only with the aqueous solution prepared in the laboratory.
- ❖ Characterization of adsorbent was done by determining surface area and Boehm's titration.
- ❖ Kinetic study was performed in lab temperature at 25 °C
- ❖ Due to unavailability of certified standard metal ion samples, chemicals available in the laboratory were used directly for their respectively concentration evaluation with careful attention as mention in the standard text.

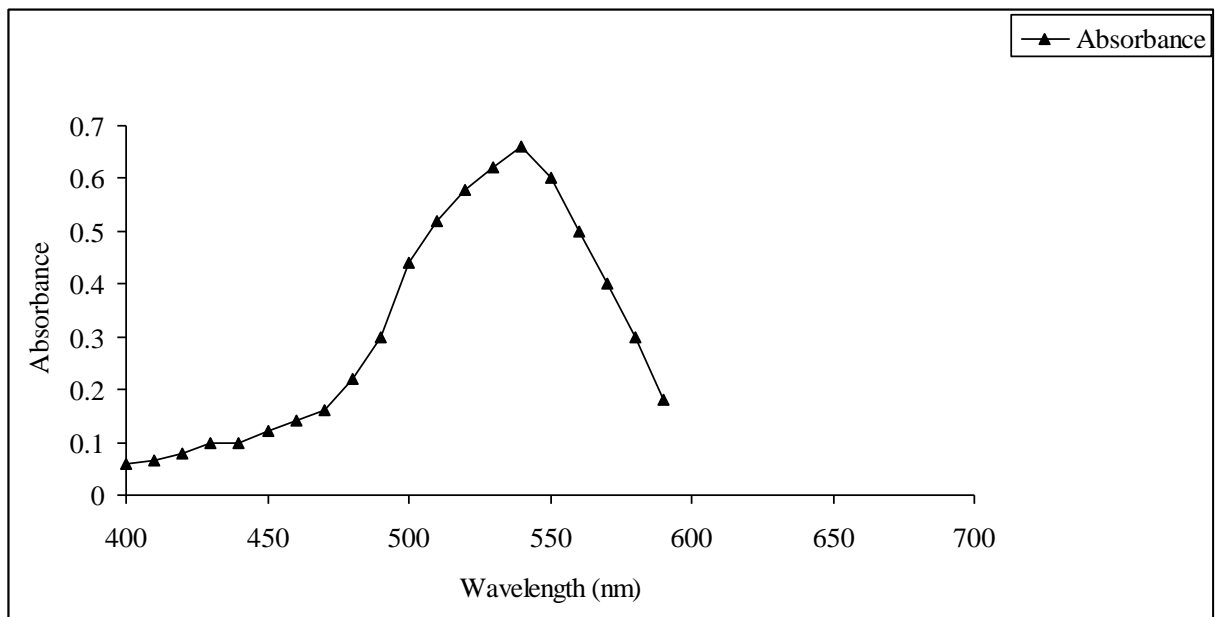


Figure 4: Plot of absorbance versus wavelength for the determination of λ_{\max} of Cr (VI) solution.

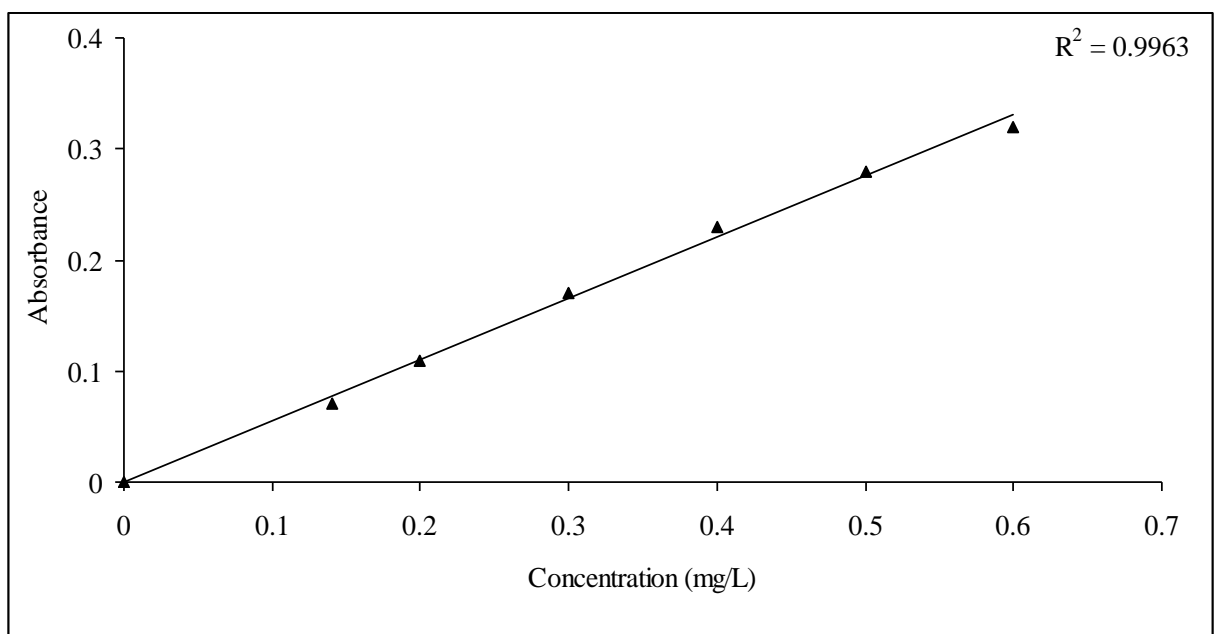


Figure 5: Calibration curve for determination of Cr (VI) in aqueous solution

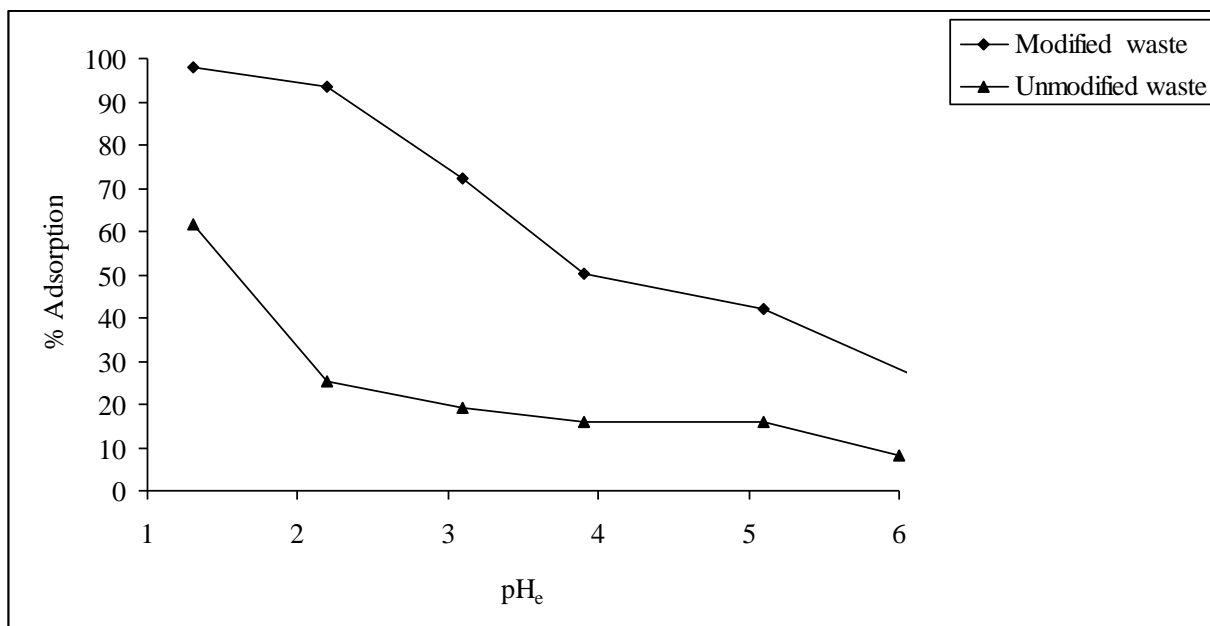


Fig 6: Effect of pH for adsorption of Cr(VI) onto modified and unmodified sugarcane waste.

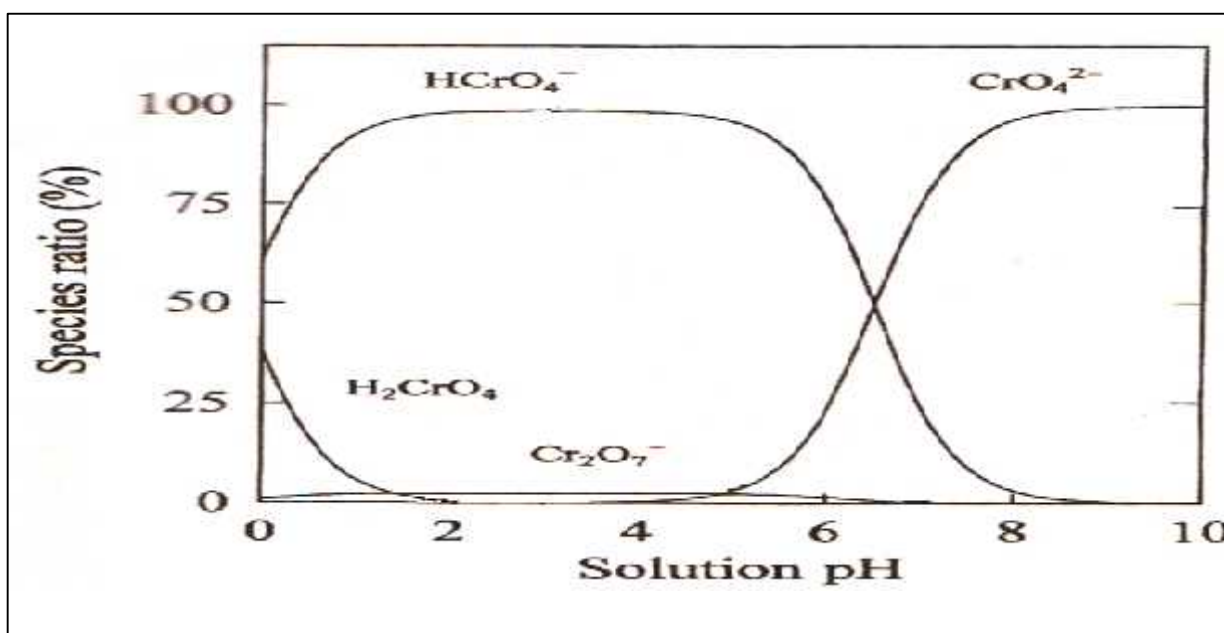


Fig 7: Distribution of chromium species in K₂Cr₂O₇ as the function of pH

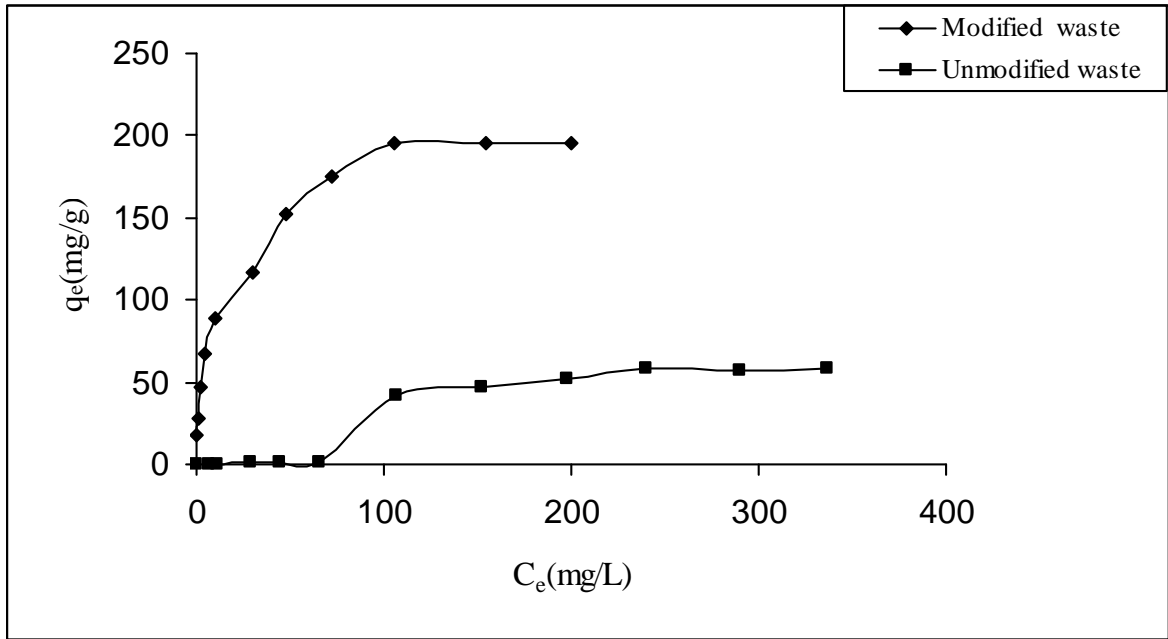


Figure 8: Adsorption isotherm for adsorption of Cr(VI) onto modified and unmodified sugarcane waste.

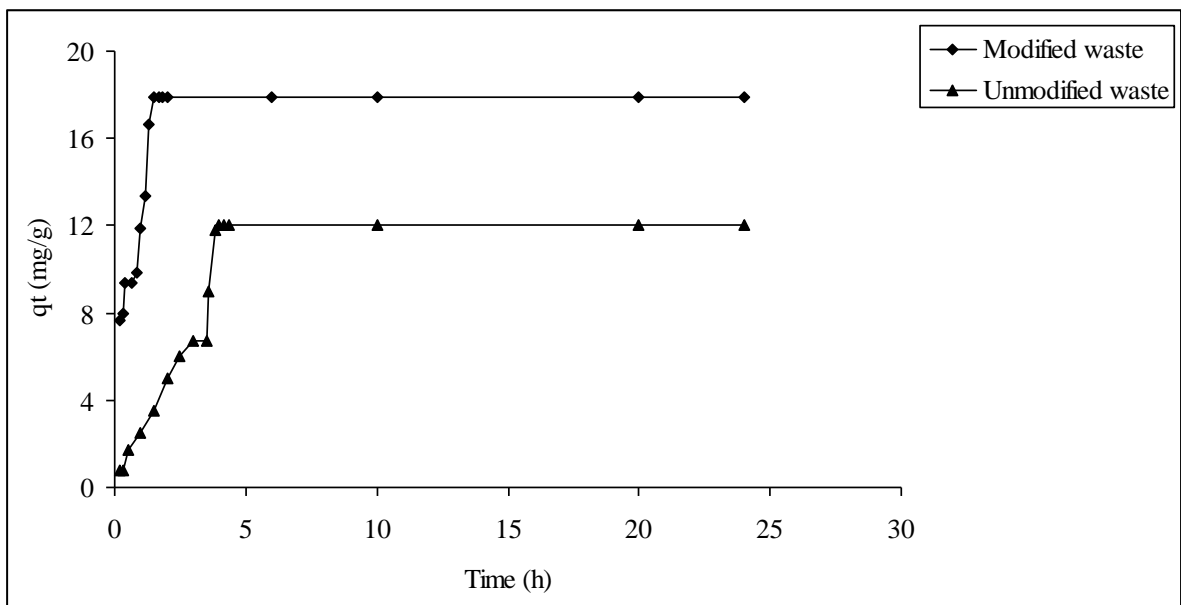


Figure 9: Effect of contact time for the adsorption of Cr(VI) onto modified and unmodified sugarcane waste.

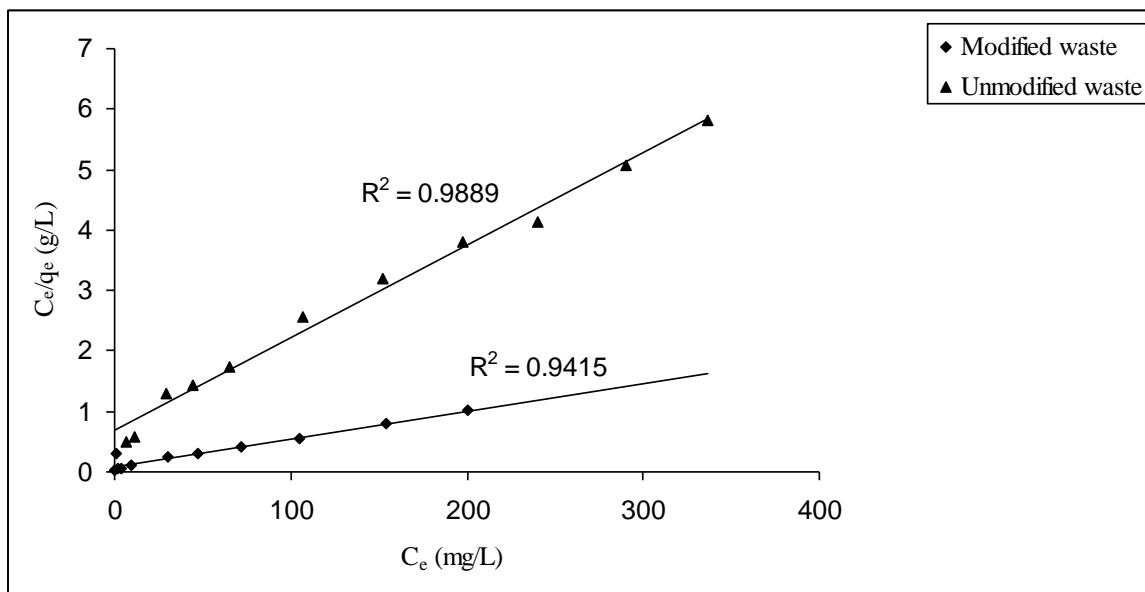


Figure 10: Langmuir isotherm plot for adsorption of Cr(VI) onto modified and unmodified sugarcane waste.

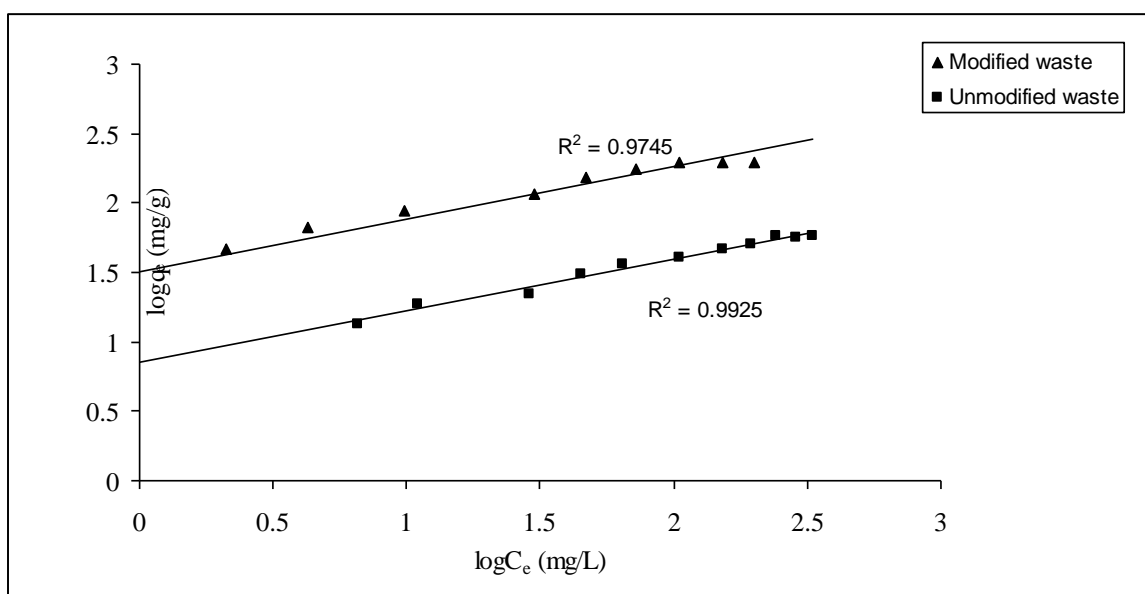


Figure 11: Freundlich isotherm plot for adsorption of Cr(VI) onto modified and unmodified sugarcane waste

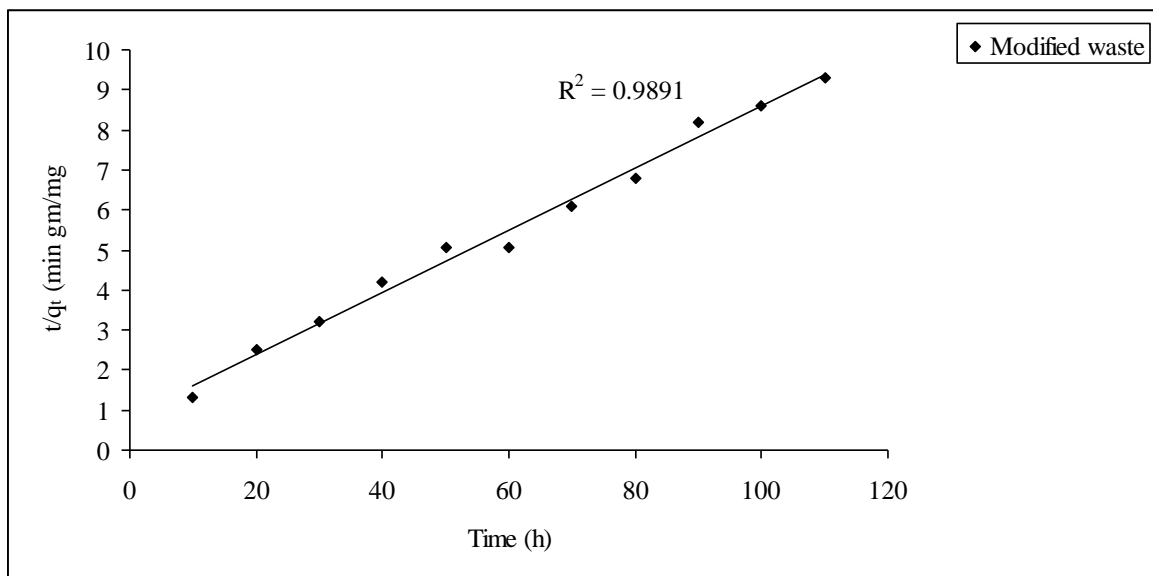


Figure 12: Pseudo-second order kinetic plot for adsorption of Cr(VI) onto modified sugarcane waste.

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APPENDIX

Table 1: Determination of }_{max} of Cr(VI) DPCI complex

S.N.	Wave length (nm)	Absorbance
1	400	0.06
2	410	0.065
3	420	0.080
4	430	0.10
5	440	0.10
6	450	0.12
7	460	0.14
8	470	0.16
9	480	0.22
10	490	0.30
11	500	0.44
12	510	0.52
13	520	0.58
14	530	0.62
15	540	0.66
17	550	0.58
18	560	0.50
19	570	0.40
20	580	0.30
21	590	0.18

Table 2: Accuracy and precision of the DPCI method for the determination of Chromium
Four replicate analysis

S.N	Concentration of Cr taken	Abs.	Concentration of Cr found	Mean	Standard deviation	95 % confidence limit
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	(μg)		(μg)			
1.	10.0	0.07	9.80	9.90	0.20	9.90 ± 0.318
	10.0	0.07	9.80			
	10.0	0.08	10.20			
	10.0	0.07	9.80			
2	20.0	0.13	20.20	19.90	0.20	19.90 ± 0.318
	20.0	0.11	19.80			
	20.0	0.11	19.80			
	20.0	0.11	19.80			
3	30.0	0.19	30.40	30.10	0.20	30.10 ± 0.318
	30.0	0.17	30.00			
	30.0	0.17	30.00			
	30.0	0.17	30.00			
4	40.0	0.23	39.80	39.90	0.20	39.90 ± 0.318
	40.0	0.23	39.80			
	40.0	0.25	40.20			
	40.0	0.23	39.80			

Table 3: Effect of pH in the adsorption of Cr(VI) metal ion onto chemically modified sugarcane waste (25 mL of solution of 20 mg/L of Cr(VI) with 25 mg of adsorbent)

pH	pH _e	Concentration mg/L	Initial concentration C _i mg/L	Equilibrium concentration	Concentration adsorbed	% A
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				C_e mg/L	mg/L	
1	1.3	20	18.75	0.375	18.357	98
2	2.2	20	19.75	1.25	18.5	88.10
3	3.1	20	19.75	5.50	14.25	72.15
4	3.9	20	19.75	9.375	10.375	50.20
5	5.1	20	18.75	10.25	8.25	42.16
6	6.1	20	18.75	13.75	5	26.66

Table 4: Effect of pH in the adsorption of Cr(VI) metal ion onto unmodified sugarcane waste (25 mL of solution of 20 mg/L of Cr(VI) with 25 mg of adsorbent)

pH	P_{H_e}	Concentration mg/L	Initial concentration C_i mg/L	Eq^m concentration C_e mg/L	Concentration adsorbed mg/L	% A
1	1.3	20	22.25	8.5	13.75	61.79
2	2.2	20	22.25	18.0	4.25	25.32
3	3.1	20	22.25	18.75	3.5	19.10
4	3.9	20	22.25	18.75	3.5	15.73
5	5.1	20	21.50	19.75	1.75	15.73
6	6.0	20	21.50	21.25	0.25	8.13

Table 5: Effect of initial concentration on the Adsorption of Cr(VI) metal ion onto chemically modified sugarcane waste (25 mL of solution of 20 mg/L of Cr(VI) with 25 mg of adsorbent)

Optimum pH	Conc ⁿ mg/L	Initial concentration C_i	Eq^m concentration C_e	Conc ⁿ adsorbed (mg/L)	q_e mg/g	C_e/q_e (g/L)	$\log C_e$ (mg/L)	$\log q_e$ mg/g

		(mg/L)	(mg/L)					
1	20	18.75	0.375	18.37	18.37	0.020	-0.425	1.26
1	30	28.875	0.875	28	28	0.031	-0.057	1.44
1	50	49.375	2.215	47.25	47.25	0.044	0.327	1.67
1	75	72	4.25	67.75	67.75	0.062	0.628	1.83
1	100	98.75	9.875	88.675	88.67	0.111	0.994	1.94
1	150	147	30.0	117	117	0.256	1.477	2.06
1	200	199	47	152	152	0.309	1.672	2.18
1	250	247	72	175	175	0.411	1.857	2.24
1	300	300	105	195	195	0.538	2.02	2.29
1	350	349	154	195	195	0.789	2.18	2.29
1	400	395	200	195	195	1.025	2.30	2.29

Table 6: Effect of initial concentration on the adsorption of Cr(VI) metal ion onto unmodified sugarcane waste (25 mL of solution of 20 mg/L of Cr(VI) with 25 mg of adsorbent)

Opti mu m pH	Conce ntratio n (C) mg/L	Initial conce ntrati on C_i mg/L	E_{q^m} concentr ation C_e (mg/L)	Conc ⁿ adsorbed (mg/L)	q_e mg/g	C_e/q_e (g/L)	$\log C_e$ mg/L	$\log q_e$ mg/g
1	20	20.5	6.75	13.75	13.75	0.49	0.82	1.13
1	30	29.92	11.20	18.72	18.72	0.59	1.04	1.27

1	60	51.25	29.0	22.25	22.25	1.30	1.46	1.34
1	75	75.96	44.71	31.25	31.25	1.43	1.65	1.49
1	100	102.0	65.0	37.0	37.0	1.75	1.81	1.56
1	150	148.2	107.0	41.5	41.5	41.5	2.57	1.61
1	200	199.0	151.8	47.2	47.2	47.2	3.21	1.67
1	250	250.0	198.0	52.0	52.0	52.0	3.80	1.71
1	300	298.0	240.0	58.0	58.0	58.0	4.13	1.76
1	350	347.0	290.0	57.0	57.0	57.0	5.08	1.75
1	400	395	337.0	58	58	58.0	5.81	1.76

Table 7: Effect contact time for the adsorption of Cr(VI) onto surface modified sugarcane waste (25 mL of solution of 20 mg/L of Cr(VI) with 25 mg of adsorbent)

Time in hours	Initial concentration C_i (mg/L)	Equilibrium concentration C_e (mg/L)	q_t mg/g
0.166	18.75	11.12	7.63
0.323	18.75	10.75	8.0
0.50	18.75	9.375	9.375
0.666	18.75	9.375	9.375
0.833	18.75	8.875	9.875
1	18.75	6.875	11.875

1.16	18.75	5.50	13.375
1.33	18.75	2.125	16.625
1.5	18.75	0.875	17.875
1.66	18.75	0.875	17.875
1.833	18.75	0.875	17.875
2	18.75	0.875	17.875
6	18.75	0.875	17.875
20	18.75	0.875	17.875
24	18.75	0.875	17.875

Table 8: Effect of contact time for the adsorption of Cr(VI) onto unmodified sugarcane waste (25 mL of solution of 20 mg/L of Cr (VI) with 25 mg of adsorbent)

Time in hours	Initial concentration C_i (mg/L)	Equilibrium concentration C_e (mg/L)	q_t mg/g
0.166	20.50	19.75	0.75
0.333	20.50	19.75	0.75
0.5	20.50	18.75	1.75
1	20.50	18.0	2.5
1.5	20.50	17.0	3.5
2	20.50	15.50	5

2.5	20.50	14.5	6
3.0	20.50	13.75	6.75
3.5	20.50	13.75	6.75
3.6	20.50	12.0	8.5
3.83	20.50	11.5	9
4	20.50	9.5	11
10	20.50	8.5	12
20	20.50	8.5	12
24	20.50	8.5	12

Table 9: Langmuir and Freundlich parameters for the adsorption of Cr(VI) onto modified and unmodified waste

Adsorbent	q _m exp. (mg/g)	Langmuir Isotherm			Freundlich Isotherm		
		q _m (mg/g)	b (L/mg)	R ²	K (mg/g)	1/n	R ²
Modified	195	201.73	0.20	0.941	22.38	0.42	0.974
Unmodified	58	63.8	0.039	0.988	6.30	0.41	0.992

Table 10: Values of Langmuir equilibrium parameter at different concentration of Cr(VI)

Modified sugarcane waste										
initial Conc ⁿ	18.75	28.87	49.37	72.0	98.7	147	199	247	300	349

(mg/L)										
K_L values	0.18	0.12	0.077	0.05	0.04	0.02	0.02	0.01	0.01	0.01
Unmodified Material of sugarcane waste										
initial Conc ⁿ (mg/L)	20.5	29.92	1.25	75.9	102	148	19 9	250	298	347
K_L values	0.55	0.46	0.33	0.25	0.20	0.147	0.1 1	0.09 3	0.0 79	0.06 8

Table 11: Kinetic Study of the adsorptions of Cr(VI) onto chemically modified sugarcane waste(25 mL of solution of 20 mg/L of Cr(VI)with 25 mg of adsorbent)

Time in minutes	q_e (mg/g)	q_t (mg/g)	$q_e - q_t$ (mg/g)	$\log(q_e - q_t)$	$\frac{t}{q_t}$ min mg/mg	$\frac{1}{q_e - q_t}$ gm/mg
10	18.375	7.63	10.745	1.031	1.31	0.093
20	28	8.0	20	1.30	2.5	0.050
30	47.25	9.375	37.875	1.578	3.2	0.026
40	67.25	9.375	58.375	1.766	4.2	0.017
50	88.675	9.875	78.8	1.890	5.06	0.012
60	117.0	11.875	105.125	2.02	5.05	0.009
70	152.0	13.375	138.625	2.14	6.07	0.007
80	175.0	16.625	185.375	2.19	6.8	0.006
90	195.0	17.875	177.125	2.248	8.2	0.005
100	195.0	17.875	177.125	2.248	8.6	0.005
110	195.0	17.875	177.125	2.248	9.3	0.005

Table 12: Pseudo second order reaction rate constant and correlation coefficient for the adsorption of Cr(VI) onto chemically modified sugarcane waste

Metal	Adsorbent	Pseudo Second Order		
Cr(VI)	Modified sugarcane waste	K ₂	v mg/gmin	R ²
		0.080	2.0	0.989

Table 13: Effect of concentration on the adsorption of chromium(VI)

S. N.	pH	Concentration(mg/L)	Initial concentration(mg/L)	Equilibrium concentration(mg/L)	Amount Adsorbed(mg/g)	% adsorption
1	1	0.5	0.523	0.001	0.522	99.8
2	1	1.0	1.10	0.007	1.093	99.3
3	1	5.0	4.875	0.044	4.831	99.09
4	1	10.0	9.975	0.15	9.825	98.49

Table 14: Comparison of maximum adsorption capacity (q_{\max}) between previous and present studied biowaste.

Biowaste	q_{\max} value (mg/g)
Lapsi seed charcoal	58.47
Sugar activated charcoal	66.66
Raw rice husk	56.0
Modified rice husk carbon	190.0
Unmodified bagasse	58.0
Modified bagasse	195.0