

# Adsorption Mechanism of Hexavalent Chromium on Biochar

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## Abstract

The adsorption mechanism of  $\text{Cr}^{6+}$  on biochar made from wood (raw carbon) was investigated by using spectrophotometer. Biochar is a low-cost sorbent that can be used to remove trace metals from water. We investigated the ability of biochar made from wood to remove aqueous hexavalent chromium ( $\text{Cr(VI)}$ ). The adsorption of  $\text{Cr}^{6+}$  by biochar was in accordance with a chemisorption process. An investigation on the adsorption characteristics of biochar for removal of  $\text{Cr(VI)}$  from aqueous solutions was studied varying various parameters such as contact time, adsorbent dose, and adsorbate concentration. The study was conducted varying contact time, adsorbent dose, and adsorbate concentration, from 0 to 120 min, for 10ppm 20ppm 30ppm 40ppm and 50ppm, and 1gm respectively. The results of this study showed that adsorption of chromium by biochar reached to equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. The percentage degradation was studied. The obtained results showed that the adsorption of chromium (VI) follows Langmuir isotherm

equation with a correlation coefficient equal to 0.981. In addition, the kinetics of the adsorption process follows the zero-order kinetics and pseudo first-order kinetics model with a rate constant value of  $0.821 \text{ min}^{-1}$ . The results indicate that this industrial waste can be employed as a low cost alternative to commercial adsorbents for removal of chromium (VI) from water and wastewater.

## Introduction

Due to their toxicity to many life forms, metal ions in the environment are a major source of concern. Unlike organic pollutants, which are mostly degraded by bacteria, metal ions do not degrade into harmless by products. The metals of immediate concern are Cr, Mn, Fe, Zn, and Cd, which are widely distributed in the materials that comprise the earth's surface.

Among these heavy metals, **chromium** is found in higher concentrations in waste from electroplating, paints, dyes, chrome tanning, paper mills, and other industries. This metal is extremely toxic. Excessive chromium exposure can cause epigastric pain, nausea, vomiting, severe diarrhoea, and hemorrhage. The maximum chromium contaminant level in drinking water is 0.05 mg/L. To remove chromium from wastewater, various conventional treatment methods such as

chemical precipitation, ion exchange, electrolytic recovery, membrane separation, floatation, and adsorption have been used over the years.

Chromium (Cr) is an essential trace element for human health and well-being. As a result of various anthropogenic activities, its contamination, particularly hexavalent chromium Cr(VI) form, has increased in both terrestrial and aquatic ecosystems over the last few decades. Chromium pollution is a major environmental threat that has a negative impact on our environment and natural resources, particularly water and soil. Excessive exposure could result in higher levels of accumulation in human and animal tissues, resulting in toxic and negative health effects. Several studies have shown that chromium is a toxic element that has a negative impact on plant metabolic activities, reducing crop growth and yield while also lowering vegetable and grain quality. As a result, it needs to be monitored in the water, soil, and crop production systems. Several useful and practical remediation technologies have been developed.

Due to its cumulative, latent, and non-degradable features, heavy metal pollution has posed a severe threat to the ecological environment and human health in recent years. Electroplating, mining, tanning, and other industrial processes produce chromium, an extremely dangerous contaminant. The United States

Environmental Protection Agency has designated chromium as a top priority contaminant due to its significant teratogenicity. Chromium is a polyvalent metal that mostly appears in the forms of  $\text{Cr}^{6+}$  and  $\text{Cr}^{3+}$ . As a result, it is critical to investigate a simple and effective method for eliminating  $\text{Cr}^{6+}$  pollution. Chemical precipitation, membrane separation, adsorption, and other procedures are used to minimise  $\text{Cr}^{6+}$  contamination. Because of its simplicity, low cost, and excellent efficiency, adsorption has gotten a lot of attention from them. As a result, it's crucial to look into a simple and effective way to get rid of  $\text{Cr}^{6+}$  contamination. To reduce  $\text{Cr}^{6+}$  contamination, chemical precipitation, membrane separation, adsorption, and other methods are applied. These traditional methods are ineffective for removing metals when they are present in low concentrations. The majority of these methods have drawbacks, such as high capital and operating costs or the disposal of residual metal sludge.

To reduce the concentration of heavy metal ions to an environmentally acceptable level, a cost-effective and efficient separation method must be developed. **Adsorption** is generally preferred over other water treatment techniques for the removal of heavy metal ions due to its high efficiency, ease of handling, availability of various adsorbents, and cost effectiveness.

Adsorption has gained a lot of attention from them because of its simplicity, low cost, and high efficiency. Many research has been carried out about the development of low-cost activated carbon adsorbents, i.e. biochar, which is made from less expensive and more readily available materials. Because of their large surface area, microporous nature, and chemical nature, activated carbons are potential adsorbents for heavy metal removal from industrial wastewater.

Biochar is a very heterogeneous material made up of inorganic (IC, ash) and organic (OC) components with different oxygen-containing functional groups.

Both components are most likely crucial in the adsorption process. Inorganic mineral composition, for example, plays a significant role in metal cation binding.

Organic substances, on the other hand, include a lot of oxygen-containing functional groups that can interact with metal ions via electrostatic attraction and surface coordination. Complexation and electrostatic adsorption with oxygen-containing functional groups in the OC, co-precipitation with inorganic mineral components, and ion exchange with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the IC are the main adsorption processes of  $\text{Pb}^{2+}$  by sludge carbon.

Redox reactions with oxygen-carrying functional groups such as hydroxyl and carboxyl in organic compounds, as well as aromatic groups containing electrons,

could convert  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ . The surface complexation of heavy metals with the COOH or OH groups of the OC resulted in the adsorption of  $\text{Cu}^{2+}$  by charcoal.

However, there are few research on how biochar components adsorb, the mechanisms by which they adsorb, and how to quantify adsorption for a specific metal ion. Pickling and high-temperature pyrolysis were used to make the OC and IC of biochar in this work.

Adsorption tests for  $\text{Cr}^{6+}$  were carried out, and biochar was analysed before and after adsorption. Using well-characterized biochar as sorbents, this work investigates the processes and effectiveness of Cr(VI) removal from solution over a period of time and Cr loading levels. Spectrophotometer analyses are carried out after the adsorption experiments to restrict the Cr valence state and binding environment at the biochar surfaces. We show the solution conditions under which Cr(VI) is removed from solution to biochar and, for the first time, we show the speciation of reductively immobilised Cr at the biochar surfaces.

A kinetic study was carried out with concentration and time as parameters.

## **Experimental**

This section explains the design of experiment adopted to accomplish the aim and objectives of the research. It discusses about the apparatus used along with the glassware and chemicals consumed during the performance of the experiment. It also discusses the procedure followed and the timeline of the completion of each stage of study and the analysis.

### **Materials and methods**

**Chemicals used:**  $K_2Cr_2O_7$ , Distilled water, biochar, 10%  $HNO_3$ , Stock solutions of  $1000\text{ mg L}^{-1}$  Cr(VI) were prepared by dissolving 282mg  $K_2Cr_2O_7$  in distilled water at 25 °C.

### **Instruments and glassware:**

50cm<sup>3</sup> Standard measuring flasks, 1000ml Standard measuring flasks, test tubes, watch glass Rotatory shaker, Spectrophotometer

### **Analysis of chromium (VI) ions**

The concentration of residual chromium (VI) ions in the sample was read spectrophotometrically by using biochar as adsorbent. One gram of biochar was

added to different concentrations for different period of time and was read at a wavelength of 372nm.

i) Chromium Adsorption experiment

All the glasswares used in the adsorption experiment were kept overnight in 10%HNO<sub>3</sub> solutions and cleaned properly to prevent metal contamination.

A standard solution of Cr(IV) was prepared was dissolving 282mg of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in minimum amount of distilled water and standardising till 1000ml in a

1000ml standard measuring flask. After the preparation of the standard solution

now solutions of different concentrations were made based on the formula of

$C_1V_1=C_2V_2$  and absorbance were measured for 10ppm,20ppm,30ppm,40ppm and 50ppm. Two readings were taken, one in the morning and the other one at

evening on the same day. Readings were recorded as follow

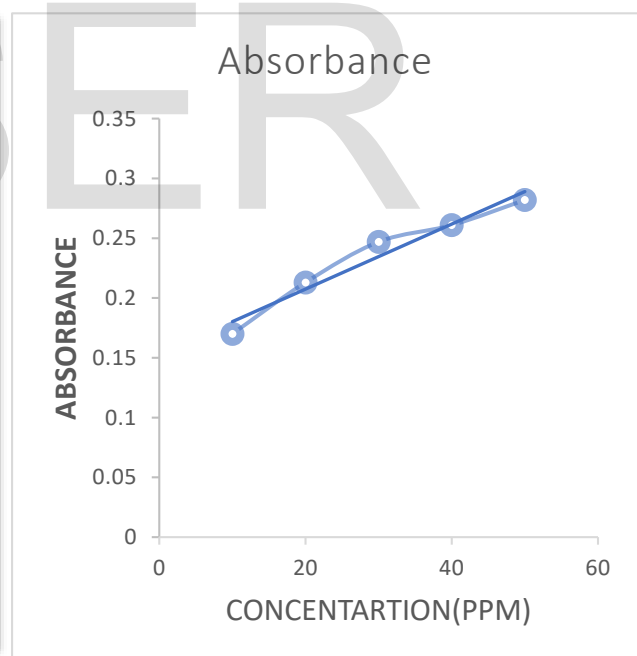
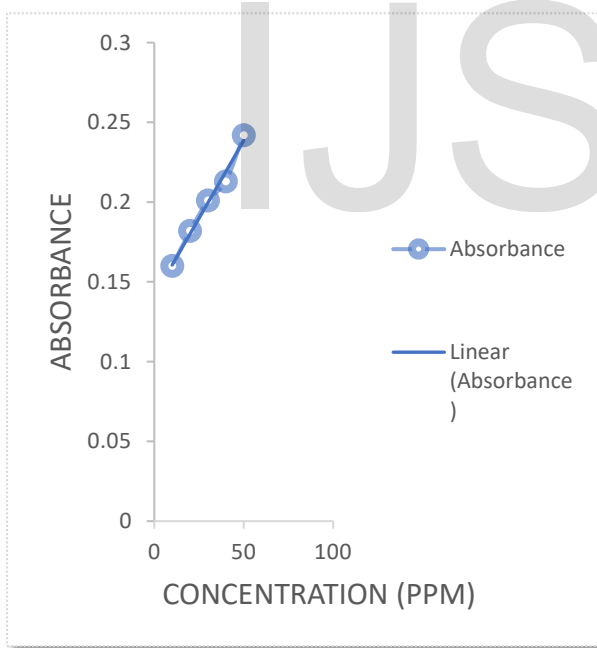
**Generating absorbance curve (Morning)**

Tube	Concentration(ppm)	Absorbance
1	10	0.16
2	20	0.182
3	30	0.201
4	40	0.213
5	50	0.242



### Generating absorbance curve (evening)

Tube	Concentration (ppm)	Absorbance
1	10	0.17
2	20	0.213
3	30	0.247
4	40	0.261
5	50	0.282



## 2. Adsorption experiment on biochar

A fixed amount of biochar i.e. 1 gm was weighed and were added to each of the concentrations prepared in a round bottle flask and that round bottom flask was kept at the rotatory stirrer for specific period of time as follow-

10 mins, 20 mins, 30 mins, 60 mins, 90 mins and 120 mins. The rate of adsorption with respect to time were measured using spectrophotometer at a wavelength of 372nm. During the experimental period, continuous mixing with a constant agitation speed was provided for better mass transfer with a high interfacial area of contact. After filtering the adsorbent with Whatman filter paper to remove biochar, the remaining concentration of chromium in each sample after adsorption was determined using a spectrophotometer and the following data were recorded-

### 1. For 10ppm

Flask	Time (mins)	Absorbance
1	10	0.701
2	20	0.601
3	30	0.543
4	60	0.419
5	90	0.304
6	120	0.2

## 2. For 20 ppm

Flask	Time(mins)	Absorbance
1	10	0.687
2	20	0.612
3	30	0.571
4	60	0.412
5	90	0.3
6	120	0.211

## 3. For 30 ppm

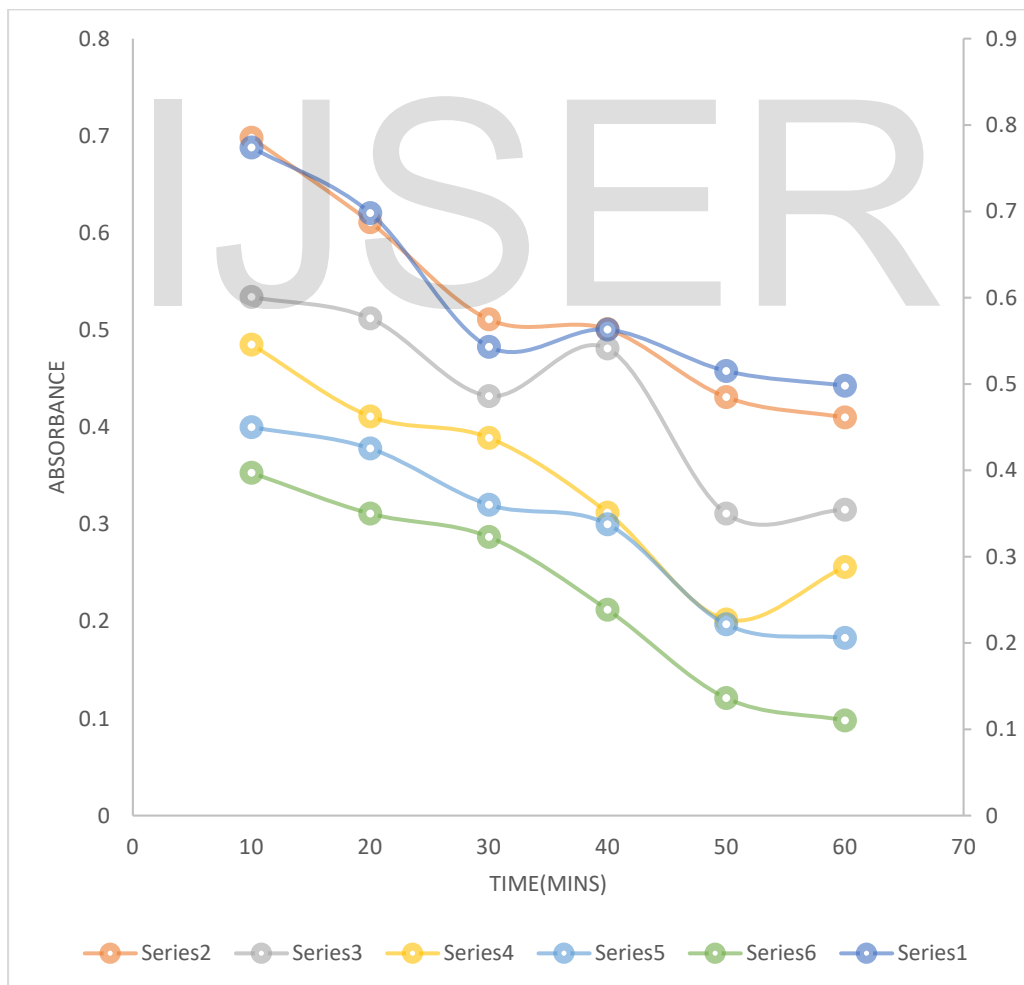
Flask	Time(mins)	Absorbance
1	10	0.543
2	20	0.511
3	30	0.465
4	60	0.398
5	90	0.291
6	120	0.217

## 4. For 40 ppm

Flask	Time(mins)	Absorbance
1	10	0.563
2	20	0.501
3	30	0.472
4	60	0.312
5	90	0.251
6	120	0.193

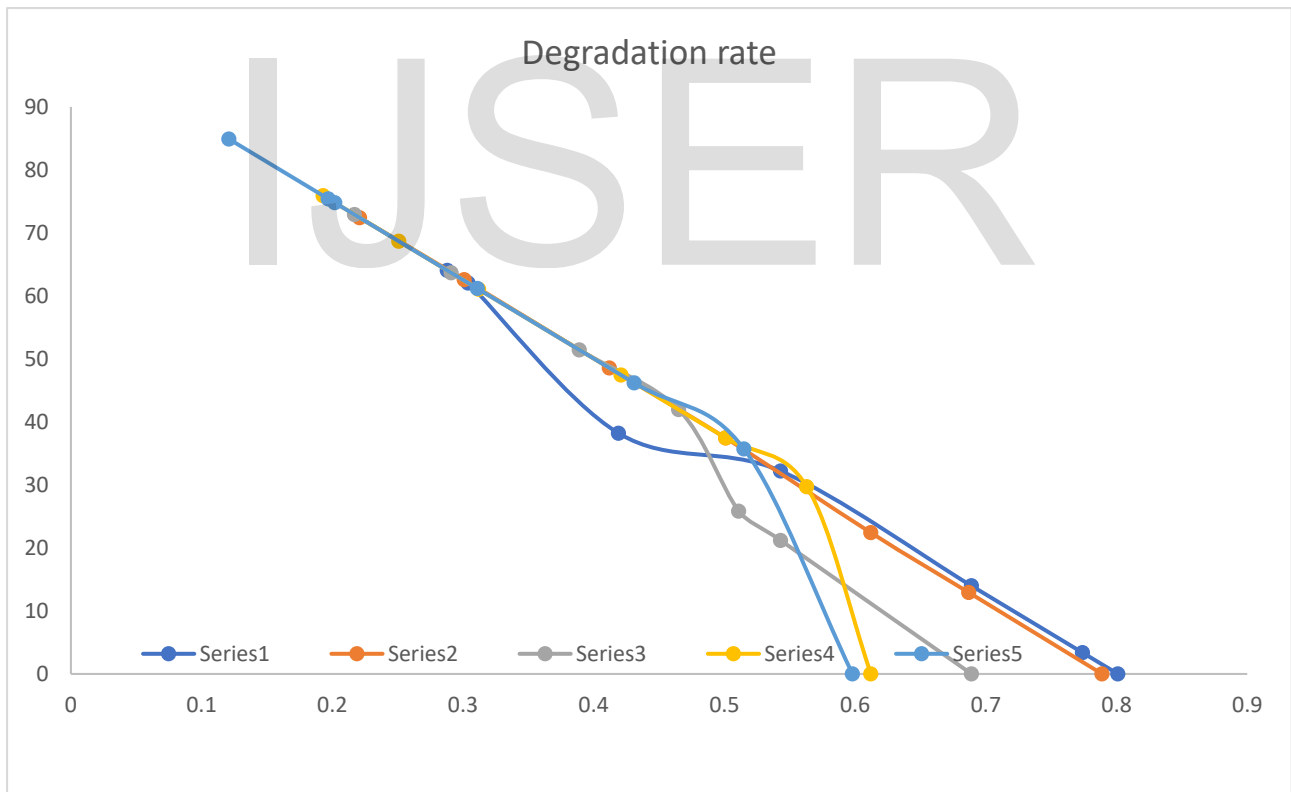
### 5. For 50 ppm

Flask	Time(mins)	Absorbance
1	10	0.515
2	20	0.431
3	30	0.311
4	60	0.202
5	90	0.197
6	120	0.121



After the measurements taken the plot of the graph has been observed and percentage of degradation were calculated and results were as follows-

sample(ppm)	10	%Degr	20	%Degr	30	%Degr	40	%Degr	50	%Degr
time(mins)										
0	0.801	0	0.79	0	0.689	0	0.61	0	0.6	0
10	0.774	3.3707	0.69	12.927	0.543	21.19	0.56	29.712	0.52	35.705
20	0.689	13.9825	0.61	22.433	0.511	25.834	0.5	37.453	0.43	46.192
30	0.543	32.209	0.5	37.453	0.465	41.947	0.42	47.44	0.31	61.173
60	0.419	38.2	0.41	48.568	0.389	51.435	0.31	61.048	0.2	74.781
90	0.304	62.047	0.3	62.576	0.291	63.67	0.25	68.664	0.2	75.405
120	0.288	64.044	0.22	72.409	0.217	72.909	0.19	75.905	0.12	84.893



## Adsorption Isotherm

Several models have been used to describe adsorption isotherm experimental data. The Freundlich and Langmuir models are the most commonly used. Both models were used in the current work. The Freundlich isotherm model describes the adsorption process in which a heterogeneous adsorbent surface participates in the multilayer distribution of the adsorbate with interaction between adsorbed molecules. The relationship between adsorbent's metal uptake capacity  $q_e$  (mg/g) and the residual metal ion concentration  $C_e$  (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + 1/n \ln C_e$$

where the intercept  $\ln k$  is a measure of adsorbent capacity, and the slope  $1/n$  is the adsorption intensity.  $k$  is related to temperature and the chemical or physical characteristics of adsorbents, where as “ $n$ ” is an indicator of the change of intensity of adsorption process and also a measure of the deviation from linearity of the adsorption. A higher value of  $n$  ( $n > 1$ ) indicates favourable adsorption, whereas  $n < 1$  represents poor adsorption characteristics. The value of  $n \approx 3.66$  suggests favourable adsorption. The situation  $n > 1$  is most common and may be due to a distribution of surface sites or any factor that cause a decrease in adsorbent eadsorbate interaction with increasing surface density. The isotherm

data fit the Freundlich model ( $R^2 \approx 0.987$ ). The Langmuir isotherm suggests monolayer adsorption on a homogeneous surface with a finite number of adsorption sites and without any interaction between the adsorbed molecules. The Langmuir equation relates solid phase adsorbate concentration ( $q_e$ ), the uptake, to the equilibrium liquid concentration ( $C_e$ ) as follows

$$q_e = \frac{K_L b C_e}{1 + b C_e}$$

where  $K_L$  and  $b$  are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively.

Isotherm type	Isotherm Constant	$R^2$
Freundlich model $k$	$(l/g)$ 0.389 $1/n$ 0.273	0.987
Langmuir model $K_L$	$(mg/g)$ 0.904 $b (l/g)$ 0.512	0.999

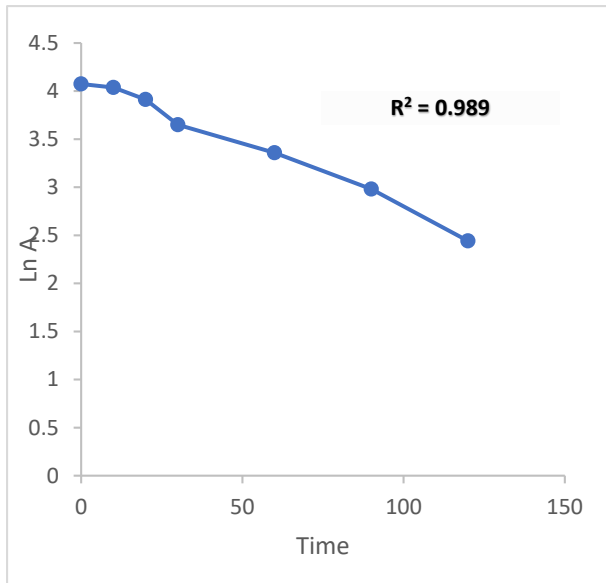
$$R_L = 1/(1+B C_{co})$$

where,  $C_0$  is the initial concentration of chromium (mg/l).  $R_L \approx 1$  represents linear adsorption, while  $R_L \approx 0$  stands for the irreversible adsorption process.  $R_L < 1$  is for favourable adsorption, while  $R_L > 1$  represents unfavourable adsorption. In this case, the value of  $R_L$  was found to be 0.975, suggesting that the adsorption process was less than 1 but it was nearly equal to 1 so it was linear adsorption.

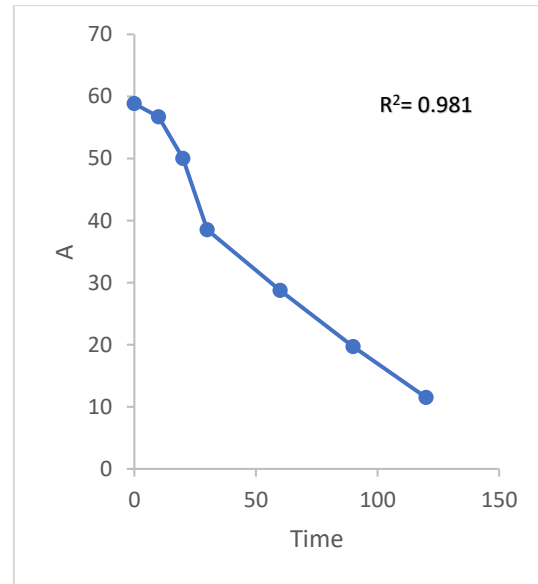
### **Adsorption Kinetic**

The kinetics parameters for the adsorption process were studied for contact times ranging from 0 to 120 min in order to define the adsorption kinetics of heavy metal ions by monitoring the removal percentage of the Cr (VI). The data was then regressed against the Lagergren equation, which represents a zero order kinetics and as well as a pseudo-first-order kinetics equation





Zero order



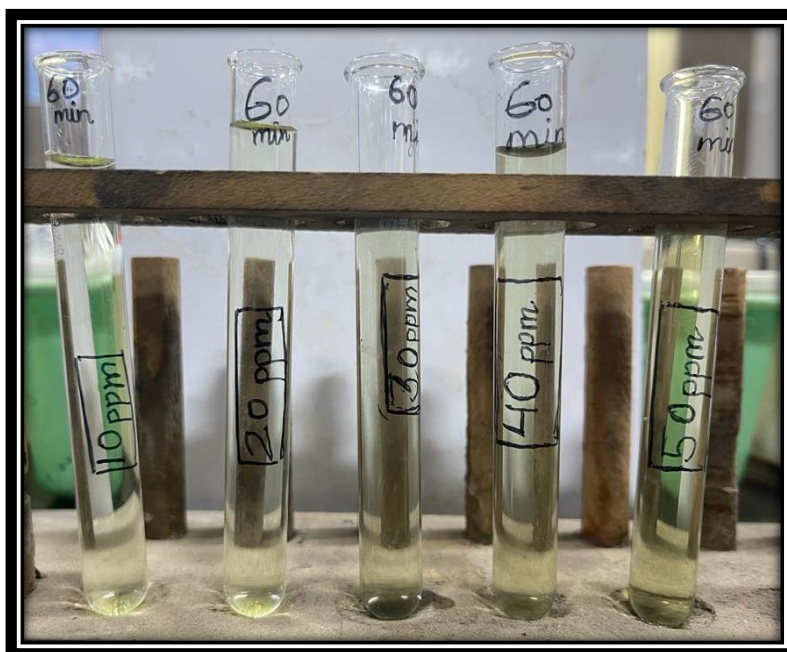
Pseudo first order

Kinetics order	R <sup>2</sup>
Zero order model	0.989
Pseudo first order model	0.981

## Photographs:



**FIG 1 Biochar used in the experiment**



**FIG 2 Calibration for different concentration**



**FIG 3 Mixture kept at Rotatory shaker**



**FIG 4 Spectrophotometer measurement at 372nm**

## **Result and Discussion**

The capability of eliminating Cr(VI) from aqueous solutions using biochar was proven in this study. The findings revealed that Cr(VI) can, however, be transformed to Cr(III) on the biochar surface. The current study demonstrates that biochar is an effective adsorbent for removing chromium (VI) from aqueous solutions. Biochar was discovered to be effective, as the removal of Cr (VI) reached 100% at room temperature.

As a result, biochar appears to be a suitable redox-active sorbent for the immobilisation of Cr (VI). The difference in coordination number in the Cr-C interatomic distances in biochar systems is influenced by the kind of biochar feedstock, pyrolysis temperature, and solution temperature.

It was also discovered that experimental parameters such as adsorbent dose, adsorbate concentration, and time have a significant impact on the adsorption process. The percentage degradation was also calculated and were observed that the rate of degradation decreases with increase in the time of stirring and concentration of the chromium biochar mixture. In the presence of other heavy metals, the adsorption efficiency will be reduced because other metal ions will compete with chromate ions. Ion affinity for the sorbent is determined by ionic

radius, electronegativity, and ionic hydrolysis constants. Although the removal of chromate ions in the presence of other ions has not been studied, it is suggested for future research by other researchers.

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