



# **Sequestration of Hexavalent Chromium from Aqueous Medium Using Biochar Prepared from Water Hyacinth Biomass**

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### **Authors' contributions**

*This work was carried out in collaboration between all authors. Author EP designed the study. Author RPP conducted the designed work, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors PM, SA and VD supervised the work. All authors read and approved the final manuscript.*

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## **ABSTRACT**

The global issue associated with the health of environment and human is the quality of water. A serious threat to the aquatic environment through anthropogenic activities is the heavy metal pollution. To protect our environment from the serious threats of contamination and to save many lives, it is essential to remove Cr from wastewater. This paper reports the utilization of the water hyacinth biochar, a carbonaceous material as adsorbent for removal of hexavalent chromium (Cr(VI)) from aqueous solution. The experiment was carried out in the Department of Environmental Sciences, Tamil Nadu Agricultural University, Coimbatore in a completely randomized design with 4 replications. The adsorbent was characterized by FTIR, SEM and EDX. The effect of various process parameters like solution pH, adsorbate concentration, contact time, adsorbent dosage and size has been studied. The optimum conditions for the removal of Cr(VI)

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were found to be pH=2.0, adsorbent size= 0.2 mm, adsorbent dosage=2.5 g/100 ml, adsorbate concentration=100 mg/L of Cr(VI) at 25°C at 250 rpm. The rate of adsorption was rapid and the equilibrium was attained at 36 hrs. Models of Langmuir, Freundlich and Temkin isotherms were used for mathematical description of the equilibrium adsorption data. Adsorption data was well described by the Langmuir isotherm with maximum adsorption capacity of 55.55 mg/g. On comparison with various kinetic models, our results fitted excellently with pseudo second order model ( $R^2=0.999$ ). It can be concluded that, carbonaceous material derived from water hyacinth biomass can be used as a low cost adsorbent for the treatment of Cr(VI) containing waste water.

**Keywords:** Adsorbate; adsorbent; chromium; concentration; isotherm.

## 1. INTRODUCTION

Release of heavy metals into the environment is a matter of global concern for the past few years and it should be removed from industrial waste waters before discharge for maintaining water quality standards. Heavy metals are trace metals, known to be most persistent and non biodegradable pollutant emanated from wide range of industries [1]. Among the heavy metals, chromium (Cr), cadmium (Cd), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and arsenic (As) are known for its environmental risk [2]. Chromium contamination is a significant obstacle worldwide due primarily of its multifarious use in industrial processes such as plating, alloying, tanning of hides, metallurgy, refractory, textile dyes, paint, chemical manufacturing and petroleum refining etc. [3]. This element (Cr) occurs naturally in rocks, soil, volcanic dust, gases etc., The Central Pollution Control Board have specified the safe limit of chromium concentration as 0.05mg/L for drinking water, 0.1mg/L for inland surface water and various industries, 1mg/L for marine coastal areas and 2mg/L for public sewers [4]. Chromium has a complex electronic and valence shell chemistry with valence states ranging from -2 to +6 [5]. Among the oxidation states of Cr, the most environmentally significant and stable forms are trivalent (Cr(III)) and hexavalent (Cr(VI)) [6]. The Cr(III) and Cr (VI) differs in mobility and toxicity. Cr(VI) is known for its mobility and carcinogenicity whereas Cr(III) is relatively immobile and less toxic [7]. So this paper focuses on the removal of Cr(VI) from aqueous solution.

Conventional methods such as membrane filtration, chemical precipitation, reduction, ion exchange, reverse osmosis and electro dialysis are available for its removal [8]. Their exorbitant nature, energy requirements and toxic sludge generation calls for an economically sound and ecologically safe technology which directed

attention towards biosorption. Biosorption is a physico-chemical process in which adsorbent concentrate and bind the contaminant onto its surface by various mechanisms like adsorption, absorption, ion exchange, surface complexation and precipitation [9]. The process parameters like solution pH, adsorbent dosage, adsorbent size, contact time, solute concentration were examined to determine the best biosorption conditions. For this novel process, water hyacinth (*Eichhornia crassipes*) is utilized as the resource base as it is the world's most prominent noxious weed grown over a wide range of aquatic environments [10]. This dreaded aquatic weed pose serious challenge to aquatic inhabitants and is often blamed for its choking nature in water bodies [11]. This study reports the utilization of water hyacinth biochar as adsorbent to remove Cr(VI) from aqueous solution.

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Adsorbents

Water hyacinth plants were collected from Vaigai dam, Theni district, Tamil Nadu, India. After collection, they were washed to remove the sediments and were dried. The dried water hyacinth plants were converted to biochar through the process of pyrolysis at 450°C for 2-3 hours. The biochar produced was pulverized to a desired size.

### 2.2 Characterization of Biosorbent

The morphology of the adsorbent was analyzed with SEM (Scanning Electron Microscope) (M/s. FEI- Quanta 250, Czech Republic) at 7.00 kV equipped with the back scattered electron detector. Energy Dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition of the adsorbent. The functional groups present in the adsorbent was identified

through Fourier transform infrared (FTIR) spectrometry equipped with a diamond tipped ATR accessory (Shimadzu, Japan) at wave number of 4000 to 400 $\text{cm}^{-1}$ . The spectra were plotted on transmittance axis before and after Cr(VI) adsorption onto water hyacinth biochar.

### 2.2.1 Zeta potential

The zeta potential was measured to determine the surface charge of the water hyacinth biochar. About 0.5mg of the adsorbent was added to 20 ml of deionised water and the suspension was shaken at 180 rpm for 2 hours using mechanical shaker. Then the suspension was left in sonic bath to break the particles into colloids and suspension was filtered through whatman no.42 filter paper. The zeta potential was determined from the supernatant by particle size analyser (Horiba Scientific Nanopartica SZ-100, Japan) [12].

### 2.3 Adsorption Experiment

Batch experiments were conducted to study the influence of varied solution pH (1 to 9), adsorbent size (0.2 to 4.0mm), adsorbent dosage (0.5 to 2.5g/100ml), adsorbate concentration (100 to 2000mg/L) and contact time (6 to 48hrs) on sorption behaviour of Cr(VI) and to establish optimum experimental strategies for adsorption process. These experiments were carried out at 25°C in 250ml conical flasks with 100ml solute volume and agitated on a rotary shaker at 250rpm. At the end of shaking period, the samples were centrifuged at 8000rpm for 10 minutes and filtered through whatman no.42 filter. The residual concentration of metal ion (Cr) was determined by atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 400). The batch experiments were carried in a completely randomized design replicated four times.

The amount of Cr(VI) ions adsorbed onto the adsorbent at equilibrium ( $q_e$ ) was calculated using the equation (1),

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of adsorbate in solution (mg/L),  $V$  is the volume of adsorbate solution taken (L) and  $M$  is the mass of the adsorbent (g) used.

The percent removal of Cr(VI) from aqueous solution was determined using the equation (2).

$$\% \text{ removal} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of adsorbate in solution (mg/L).

### 2.3.1 Point of zero charge of *E. crassipes*

Point of zero charge ( $\text{pH}_{\text{ZPC}}$ ) was determined using solid addition method [13]. This experiment was carried out by taking solution of 0.1M  $\text{KNO}_3$  (50ml) with the pH of the solution adjusted from 2 to 10 ( $\text{pH}_{\text{initial}}$ ) by adding 0.1N  $\text{HNO}_3$  or 0.1N  $\text{NaOH}$  and then 1.0g of biochar was added. The mixture was then manually agitated and allowed to equilibrate for 48hrs and centrifuged at 5000rpm for 5 minutes and then change in pH of solution ( $\text{pH}_{\text{final}}$ ) was measured. The difference between initial and final pH ( $\Delta\text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$ ) was plotted against  $\text{pH}_{\text{initial}}$  and the point of intersection gave  $\text{pH}_{\text{ZPC}}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of Biosorbent

The results regarding the characteristics of water hyacinth biochar is furnished in Table 1. The pH of the biochar was found to be alkaline (9.83) with EC of 3.90 $\text{dSm}^{-1}$ . The cation exchange capacity was high with negative zeta potential which suggests the dominancy of the adsorbent surface with negative charges.

### 3.2 Point of Zero Charge of Water Hyacinth Biochar

The sorption of metal ions depends on surface chemistry of the adsorbents where the zero point charge is a useful parameter. The point of zero charge is the pH at which the net charge on adsorbent surface is zero, having positively charges as that of negatively charged surface functions [14].

The plot between  $\Delta\text{pH}$  and  $\text{pH}_0$  (Fig. 1) shows that the pH at point of zero charge of water hyacinth biochar is 3.7. The adsorbent surface modifies its polarization according to the solution pH [15]. At  $\text{pH} > \text{pH}_{\text{ZPC}}$ , the surface of the adsorbent become negatively charged due to the sorption of  $\text{OH}^-$  by electrostatic attractive force whereas when  $\text{pH} < \text{pH}_{\text{ZPC}}$ , adsorbent surface attains positive charge due to the adsorption of  $\text{H}^+$  [16]. Hence, the adsorption of anionic metals (Cr(VI)) will be favoured at  $\text{pH} < \text{pH}_{\text{ZPC}}$  [17].

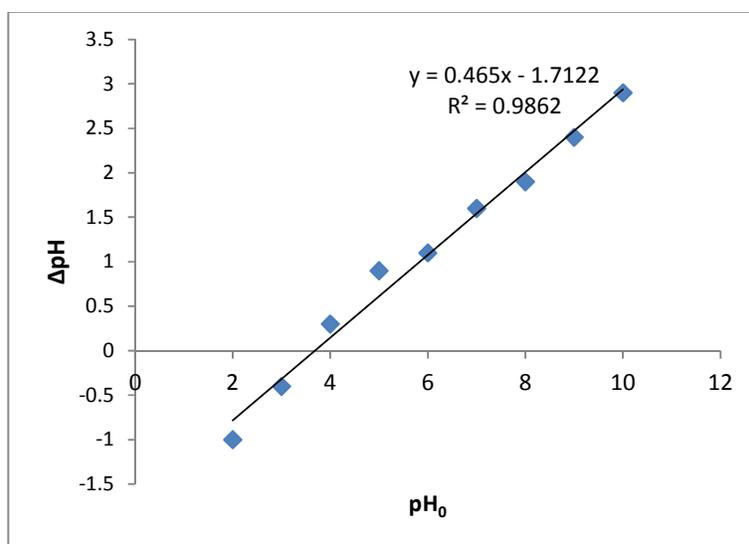
### 3.3 SEM and FTIR Analysis of Adsorbents

The surface morphology of the adsorbent was examined by scanning electron microscope (Fig. 2). A clear texture of the biosorbent material before Cr(VI) adsorption is depicted in Fig. 2a which provides a large surface for the adsorption of Cr whereas Fig. 2c depicts a rough aggregated surface of the adsorbent after Cr adsorption. This difference in surface morphology may be attributed by the agglomeration of Cr ions on the surface of the adsorbent loaded with Cr(VI) [18]. The EDX spectra of biochar before and after Cr(VI) adsorption were given in Fig. 2b and d. The peaks of Ca, O, C indicated the presence of functional groups such as -OH and -COOH in the adsorbent [19]. Adding this, the spectra of biochar before Cr(VI) adsorption showed no prominent peaks of Cr, whereas the spectra after Cr(VI) adsorption produced prominent Cr peaks with the reduction in Ca peaks [20].

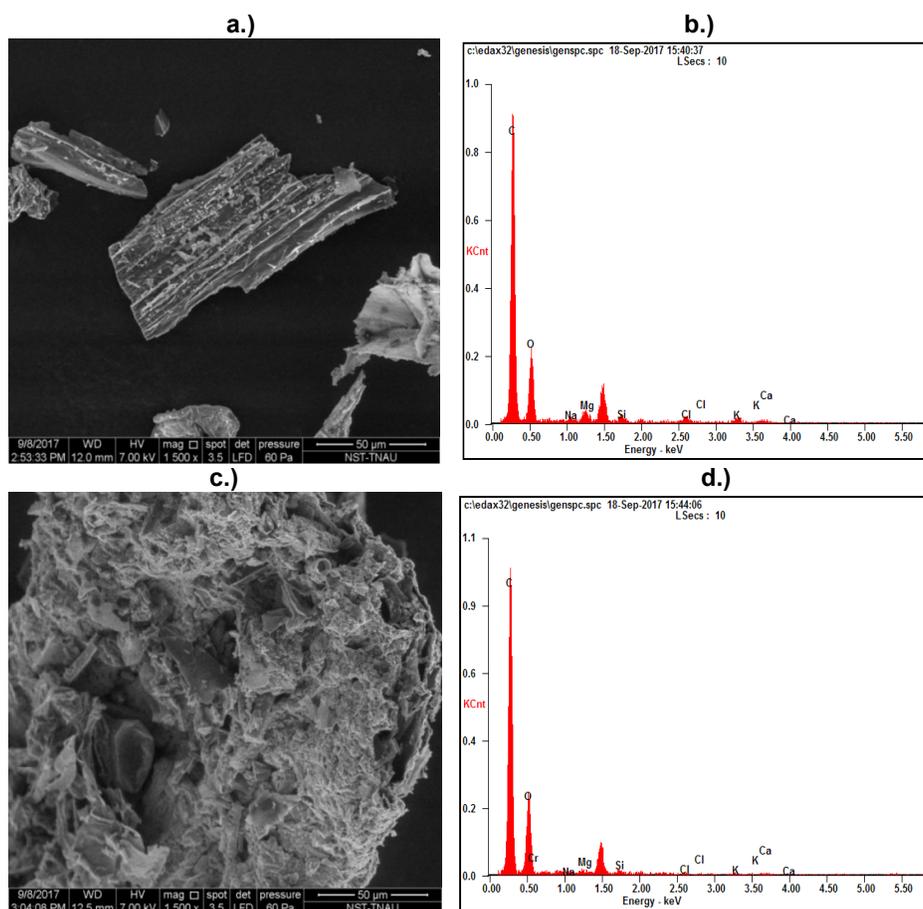
For interpretation of functional groups involved in the binding of Cr(VI), FTIR analysis was carried out with the spectra of the adsorbents measured in the range of 4000-400 $\text{cm}^{-1}$  wavenumber (Fig. 3a and b). Table 2 shows the FTIR absorption peaks of native and Cr(VI) loaded biochar which confirmed the existence of several functional groups on the surface of adsorbent. The FTIR spectra of biochar before Cr(VI) adsorption showed intense peaks at 3321.78  $\text{cm}^{-1}$  representing -OH groups which on Cr(VI) loading gets shifted to 3349.75  $\text{cm}^{-1}$ . The peak at 2319.95  $\text{cm}^{-1}$  in biochar might be due to the N-H band which gets disappeared in Cr(VI) loaded adsorbent confirming the indulgence of that functional group in Cr(VI) binding. The peaks observed at 1024.02, 1581.34 and 2119.39  $\text{cm}^{-1}$  in unloaded water hyacinth biochar can be assigned to C-O, C=O, C=C bands respectively. These peaks had been shifted to 1023.05, 1583.27 and 2162.78  $\text{cm}^{-1}$  respectively in Cr(VI) loaded biosorbent.

**Table 1. Characteristics of water hyacinth biochar**

S. No	Parameters	
1	pH	9.83
2	EC ( $\text{dSm}^{-1}$ )	3.90
3	Total organic carbon (%)	9.1
4	Cation exchange capacity ( $\text{cmol (p}^+) \text{kg}^{-1}$ )	17.5
5	Zeta potential (mV)	-21.3



**Fig. 1. Point of Zero charge of water hyacinth biochar**



**Fig. 2. a.) Scanning electron micrographs of water hyacinth biochar before Cr(VI) loading, b.) EDX spectra of water hyacinth biochar before Cr(VI) loading, c.) Scanning electron micrographs of Cr(VI) loaded biochar, d.) EDX spectra of Cr(VI) loaded biochar**

**Table 2. FTIR absorption peaks ( $\text{cm}^{-1}$ ) of native and Cr (VI) loaded WHB**

Adsorbent	-OH	C-O	C=O	N-H	C≡C
WHB	3321.78	1024.02	1581.34	2319.95	2119.39
WHB loaded with Cr(VI)	3349.75	1023.05	1583.27	-	2162.78

\*WHB- Water Hyacinth Biochar

From the FTIR spectral data, it is clear that -OH, C-O, C=O, N-H, C≡C groups were present on the surface of the adsorbent. The shifting of these functional groups and disappearance of prominent bands of several functional groups confirms the involvement of such functional groups in Cr(VI) binding onto the biochar.

### 3.4 Effect of pH

The solution's pH is one of the prominent factor which affects the Cr(VI) adsorption onto the

adsorbent. The pH dependence for Cr(VI) adsorption onto adsorbent was studied at varied pH levels viz., 1,2,3,4,5,6,7,8,9 (Fig. 4), where the optima occurred at pH 2.0 (96.25%). The changes in percent removal of Cr(VI) at different pH had been observed, which might be attributed by factors like charge of the metal ion in aqueous solution and charge on adsorbent surface at particular pH. In aqueous solution, Cr(VI) exists as anion ( $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ , or  $\text{Cr}_2\text{O}_7^{2-}$ ) [21]. The maximum adsorption of Cr(VI) at pH 2.0 might be due to the fact that at

lower pH the surface of the adsorbent acquires a positive charge which can easily bind negatively charged Cr(VI) through electrostatic force of attraction [22,23].

### 3.5 Effect of Adsorbent Size

To analyze the effect of adsorbent size in adsorption process, batch experiments were conducted at fixed adsorbate concentration of 200 mg/L Cr(VI) with varying adsorbent sizes such as 0.2, 0.5, 1.0, 2.0, 4.0 mm. The size of the adsorbent has a significant influence on the percent removal of Cr(VI) as shown in Fig. 5. Among different sizes of adsorbent, biosorbent size of 0.2mm recorded the maximum removal of Cr(VI) (96.55%) which was statistically on par performance with adsorbent size of 0.5 mm (95.15%). Higher adsorption by smaller size of the adsorbent might be due to the fact that,

decrease in particle size increases the surface area and the number of binding sites for adsorption [24].

### 3.6 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of Cr(VI) from aqueous solution is presented in Fig. 6. The batch experiment were conducted at fixed adsorbate concentration of 200 mg/L , pH of 2.0, 0.2 mm adsorbent size with a dosage of 0.5 to 2.5 g/100ml with 0.5g intervals. It is obvious from the figure that adsorption rate of Cr(VI) increased from 80.80% to 96.60% for adsorbent dose from 0.5 to 2.5g. This might be due to the fact that, increasing dosage of biosorbent in the aqueous solution increased the active sites and surface area available for adsorption [25].

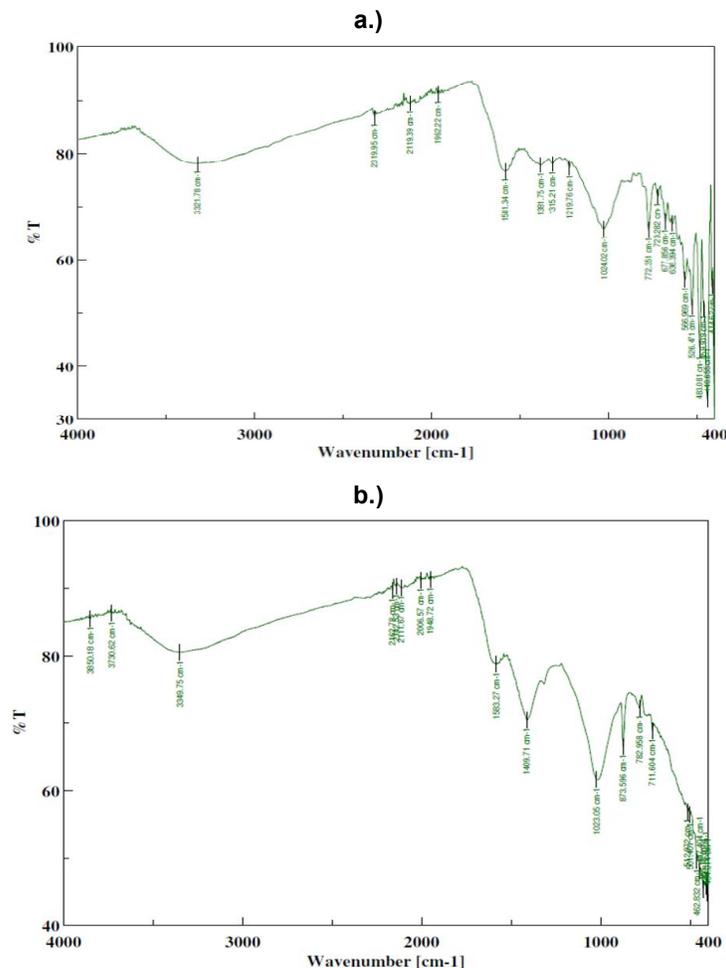
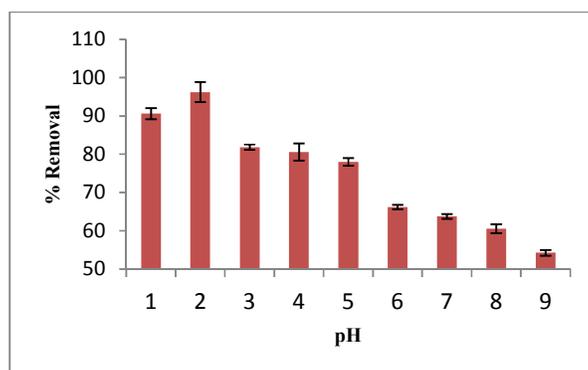
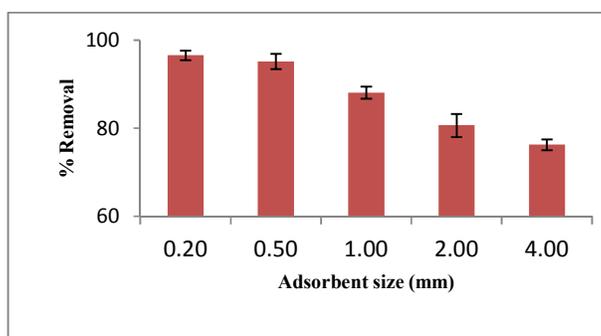


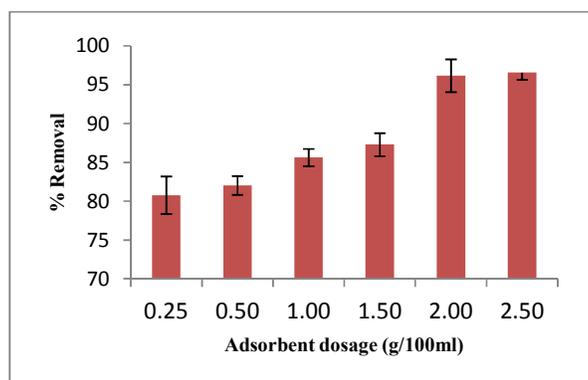
Fig. 3. FTIR spectra of water hyacinth biochar a.) before Cr adsorption, b.) after Cr(VI) adsorption



**Fig. 4. Effect of solution pH on Cr(VI) adsorption**



**Fig. 5. Effect of adsorbent size on Cr(VI) adsorption**



**Fig. 6. Effect of adsorbent dosage on Cr(VI) adsorption**

### 3.7 Effect of Adsorbate Concentration

Adsorption of Cr(VI) with regard to the effect of solute concentration was studied at the range of 100 to 2000 mg/L Cr(VI) with 100 mg/L intervals and the experiment was conducted in batch process with fixed parameters of pH= 2.0, adsorbent size=0.2 mm, adsorbent dosage=2.0g.

Fig. 7 illustrates the adsorption of Cr(VI) ions by water hyacinth biochar as a function of initial adsorbate concentration. The results showed that, maximum removal of 99.42% was recorded with 100 mg/L solute concentration beyond that the metal removal went down to 52% (2000 mg/L). This decrease in % removal with increase in solute concentration might be due to the lack

of available active binding sites required for high solute concentration of aqueous solution [26,27].

### 3.7.1 Adsorption isotherms

The data obtained were fitted to Langmuir, freundlich and temkin isotherms.

Langmuir adsorption isotherm is valid for the formation of a monolayer adsorbate on the adsorbent surface and it is given by the equation (3),

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where  $q_m$  is the maximum monolayer coverage capacity (mg/g),  $q_e$  is the amount of Cr(VI) adsorbed per gram of adsorbent at equilibrium (mg/g),  $C_e$  is the equilibrium concentration of adsorbate (mg/L) and  $K_L$  is the langmuir adsorption constant related to the affinity of binding sites (L/mg). The values of  $q_m$  and  $K_L$  were obtained from slope and intercept of plot between  $C_e/q_e$  Vs  $C_e$  [28]. The Dimensionless constant separation factor ( $K_R$ ) can be used to express the essential characteristics of Langmuir isotherm and is given by the equation (4) [29]

$$K_R = \frac{1}{1 + K_L C_0} \quad (4)$$

Where  $K_L$  and  $C_0$  has been already explained above.

The freundlich isotherm equation, which is commonly used for describing adsorption on heterogenous surface is represented by the equation (5) [30].

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where  $K_F$  is the constant related to adsorption capacity (mg/g) and  $n$  is the intensity of adsorbent. The values of  $n$  and  $K_F$  were obtained from slope and intercept of freundlich plot of  $\log q_e$  Vs  $\log C_e$ . The favourability of adsorption is indicated by the magnitude of the exponent 'n'. It is stated that adsorption characteristics is good (if  $n=2-10$ ), moderately difficult (if  $n=1-2$ ) and poor (if  $n<1$ ) [31].

Temkin isotherm is used for heterogenous surface energy systems and this isotherm assumes the heat of adsorption which is the function of temperature [32] and its adsorption equation (6) is furnished below.

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \quad (6)$$

$$B = \frac{RT}{b}$$

Where  $R$  is the universal gas constant (8.314 J/mol/K),  $T$  is the temperature (25°C),  $b$  is the temkin isotherm constant,  $A$  is the temkin isotherm equilibrium binding constant (L/g) and  $B$  is the constant related to heat of sorption (J/mol). The values of  $B$  and  $A$  were obtained from slope and intercept of temkin plot between  $q_e$  and  $\ln C_e$ .

The isotherm plots for the adsorption of Cr(VI) was shown in Fig. 8. The parameters of isotherm models calculated from the experimental data were shown in Table 3. The freundlich isotherm model showed  $R^2$  value of 0.940 for Cr(VI). The 'n' value (2.89) in the range of 2–10 indicates favourable adsorption of Cr(VI), this being the case for water hyacinth biochar studied presently (Table 3). Higher  $R^2$  value of 0.995 was obtained for Langmuir isotherm model, which

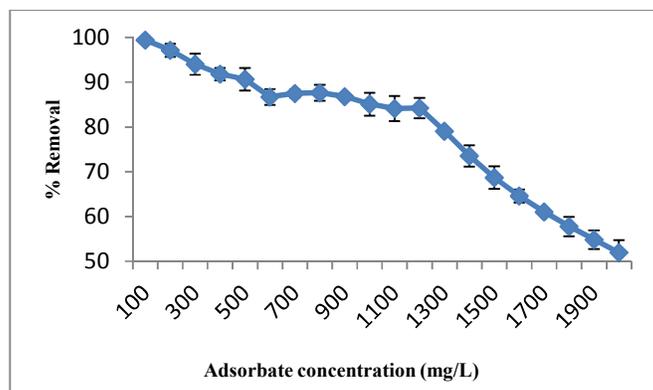
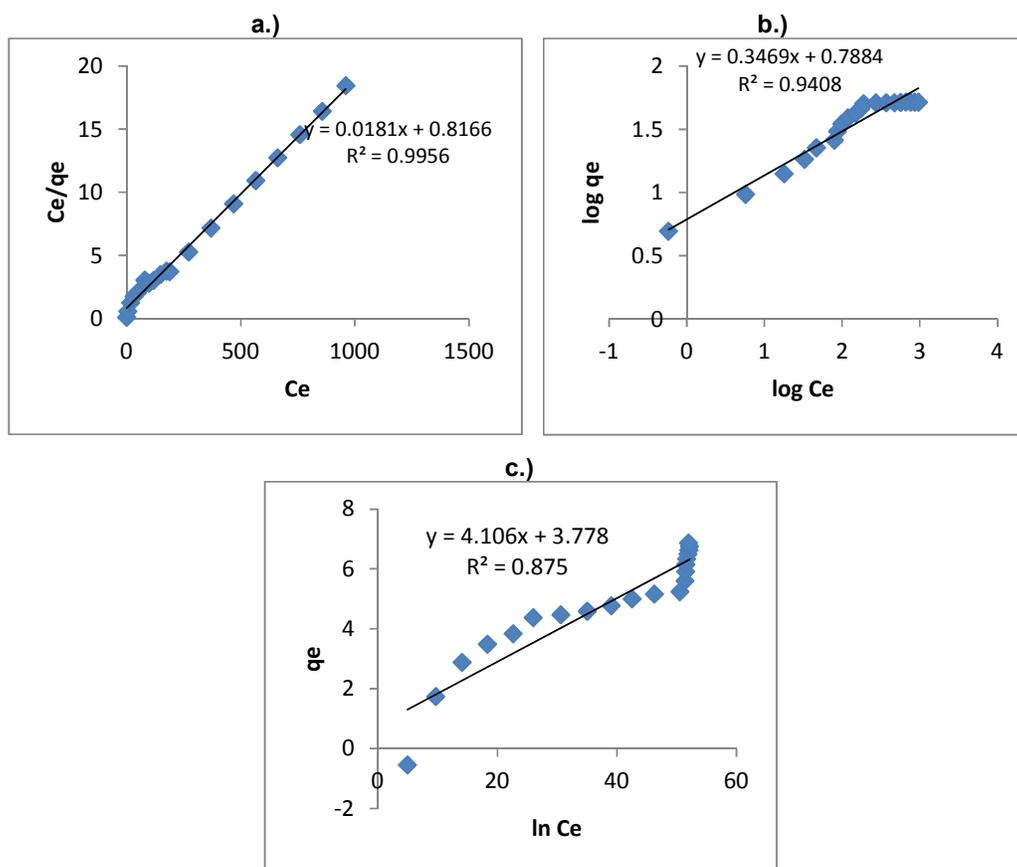


Fig. 7. Effect of adsorbate concentration on Cr(VI) adsorption



**Fig. 8. Isotherm plots for adsorption of Cr(VI) onto water hyacinth biochar a.) Langmuir isotherm, b.) Freundlich isotherm, c.) Temkin isotherm**

confirmed that adsorption of Cr(VI) onto biochar occurred onto the active sites as monolayer [33]. The  $K_R$  values for each of the solute concentration was found to be between 0 and 1, indicating favourable adsorption of Cr(VI) onto the water hyacinth biochar (Table 4). The maximum monolayer adsorption capacity ( $q_m$ ) of 55.55 mg/g was reported for water hyacinth biochar and it has been compared with different adsorbents as given in Table 5. The comparison showed that the adsorption capacity of water hyacinth biochar is comparatively higher than many other adsorbents utilized in the recent past. The experimental data for Cr(VI) adsorption was also described by temkin isotherm.

### 3.8 Effect of Contact Time

The amount of Cr(VI) adsorbed with respect to the effect of contact time was studied within the range of 6hrs to 48hrs (Fig. 9). The maximum adsorption of Cr(VI) (81.60%) occurred at 6 hrs and at equilibrium (36hrs) 97.4% of Cr(VI) was

removed. The initial rapid adsorption might be due to large number of active sites available for adsorption [34] and after a lapse of time, the remaining active sites were difficult to be occupied due to repulsive action between solute molecules of solid and bulk phases [35].

**Table 3. Isotherm constants for adsorption of Cr (VI) to water hyacinth biochar**

Constants	
<b>Langmuir isotherm</b>	
$q_m$ (mg/g)	55.55
$K_L$ (L/mg)	0.022
$R^2$	0.995
<b>Freundlich isotherm</b>	
$n$ (L/mg)	2.89
$K_F$ (mg/g)	6.14
$R^2$	0.940
<b>Temkin isotherm</b>	
$B$ (J/mol)	4.16
$A_1$ (L/g)	2.51
$R^2$	0.875

**Table 4. Values of Langmuir dimensionless constant ( $K_R$ )**

$C_0$ (mg/L)	$K_R$
100	0.313
200	0.185
300	0.132
400	0.102
500	0.083
600	0.070
700	0.061
800	0.054
900	0.048
1000	0.043
1100	0.040
1200	0.036
1300	0.034
1400	0.031
1500	0.029
1600	0.028
1700	0.026
1800	0.025
1900	0.023
2000	0.022

**3.8.1 Adsorption kinetics**

The rate of adsorption and its mechanisms were elucidated through kinetic studies. To analyze the adsorption kinetics of Cr(VI), the pseudo first order, pseudo second order, elovich and intra particle diffusion models were applied.

The pseudo first order equation or Lagergren rate equation is represented by the equation (7),

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (7)$$

Where  $q_e$  and  $q_t$  are the amounts adsorbed at equilibrium and at time  $t$  (mg/g),  $K_1$  is the rate constant of pseudo first order adsorption (1/min). The value of  $\log(q_e - q_t)$  was plotted against  $t$ . From the resulting linear relationship,  $K_1$  and  $q_e$  were determined from the slope and intercept of the plot respectively [52].

The pseudo second order kinetic equation is given by the equation (8),

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where  $K_2$  is the rate constant of pseudo second order rate equation (g/mg min). The plot of  $t/q_t$  and  $t$  gives a linear relationship. The values of  $q_e$  and  $K_2$  are obtained from slope and intercept respectively.

The elovich model equation is expressed in equation (9) as,

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha \beta) + \left(\frac{1}{\beta}\right) \ln t \quad (9)$$

Where  $\alpha$  is the initial adsorption rate (mg/g min) and  $1/\beta$  is the number of sites available for adsorption (mg/g). The values of  $\beta$  and  $\alpha$  were obtained from the slope and intercept of plot  $q_t$  and  $\ln(t)$ .

**Table 5. Cr(VI) adsorption capacity of different adsorbents**

Adsorbent	Adsorption capacity (mg/g)	Reference
Banana peel	131.56	[36]
Groundnut hull (modified)	131.00	[37]
Cyanobacteria biomass	103.09	[38]
Biomass of <i>Canna indica</i>	71.43 (at temperature 30°C)	[39]
Saw dust activated carbon	65.80	[40]
<i>Melaleuca diosmifolia</i> leaves	62.50	[41]
Treated newspaper	59.88	[42]
Water hyacinth biochar	55.55	This study
Sunflower stem waste	47.3	[43]
Rice husk carbon	45.6	[44]
Coconut husk fibre carbon	29.0	[45]
Activated carbon from <i>Syzygium jambolanum</i> nut	27.2	[46]
Sugarbeet pulp carbon	24.20	[47]
Coconut shell carbon	20.0	[48]
Mango kernel activated carbon	7.80	[49]
Potato peelings	3.28	[50]
Silica sand coated with groundwater treatment residuals	0.27	[51]

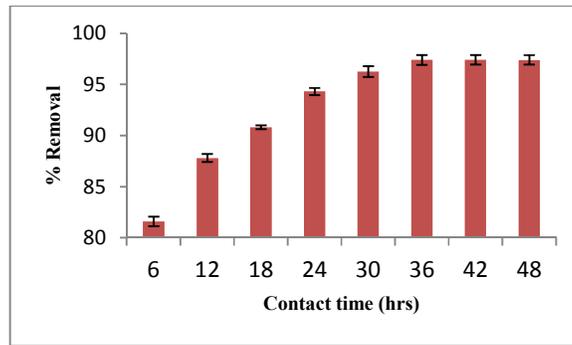


Fig. 9. Effect of contact time on Cr(VI) adsorption

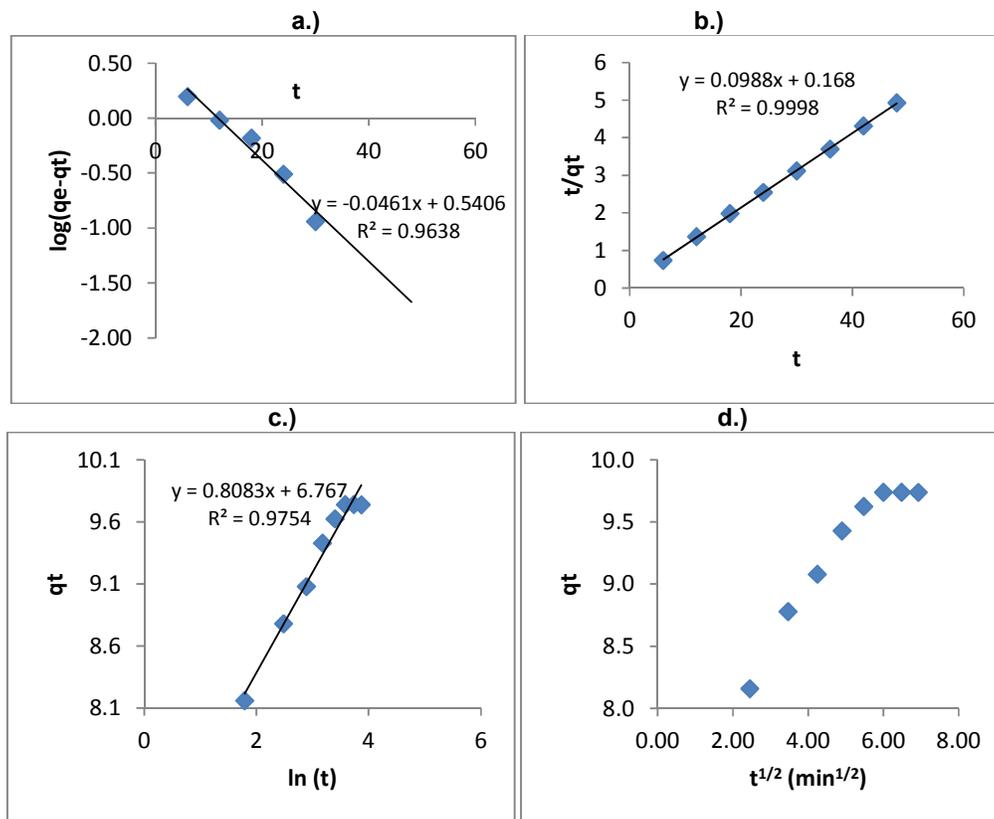


Fig. 10. Kinetic plots for adsorption of Cr (VI) onto water hyacinth biochar a.) Pseudo first order kinetic model, b.) Pseudo second order kinetic model, c.) Elovich model and d.) Intraparticle diffusion model

The diffusion mechanism is elucidated by intra particle diffusion model and it is given by equation (10),

$$q_t = K_{id}t^{1/2} + C_i \quad (10)$$

Where  $K_{id}$  is the intra particle diffusion rate constant (mg/g min) and  $C_i$  is the constant related to thickness of boundary layer (mg/g).

The value of  $C_i$  is obtained from the intercept of plot between  $q_t$  and  $t^{1/2}$ .

The data obtained from the adsorption kinetic study were furnished in Table 6. According to that, the high  $R^2$  value of 0.999 for Cr(VI) were obtained from pseudo second order kinetic model. Also, the calculated value of  $q_e$  obtained from pseudo: second order model was closer to

the experimental  $q_e$  value in pseudo second order model. For instance, the  $q_e$  calculated of Cr(VI) were 10.20 mg/g respectively were in close agreement with experimental  $q_e$  of 9.740, but for pseudo first order model, the calculated  $q_e$  value differs greatly from the experimental  $q_e$  value. The elovich equation was also employed to study the adsorption phenomena. The  $R^2$  and  $q_e$  value of pseudo second order model suggests that the adsorption of Cr(VI) by water hyacinth biochar could be better described by chemisorption [53] which involves sharing of electrons between adsorbents and adsorbate [54]. To obtain valid information pertaining to process involved in the adsorption mechanism, the data were further examined by intra particle diffusion model (Fig. 10d). The twin linear plots were obtained from diffusion model which shows that two steps were involved in the sorption process [55]. The first linear portion represents the boundary layer diffusion of solute molecules to the external surface of the adsorbent while the second linear portion represents the intra particle diffusion [56].

**Table 6. Kinetics constants for adsorption of Cr (VI) to water hyacinth biochar**

Constants	
<b>Pseudo first order model</b>	
$(q_e)_{exp}$ (mg/g)	9.740
$(q_e)_{cal}$ (mg/g)	3.467
$K_1$ (min <sup>-1</sup> )	0.106
$R^2$	0.963
<b>Pseudo second order model</b>	
$(q_e)_{exp}$ (mg/g)	9.740
$(q_e)_{cal}$ (mg/g)	10.20
$K_2$ (g/ mg. min)	0.057
$R^2$	0.999
<b>Elovich model</b>	
$\alpha$ (mg/g min)	$3.501 \times 10^3$
$\beta$ (g/mg)	1.238
$R^2$	0.975
<b>Intraparticle diffusion model</b>	
$K_{id}$ (mg/g min)	0.358
$C_i$	7.494

#### 4. CONCLUSION

This study shows that water hyacinth biochar adsorbs Cr(VI) ions to a greater extent. The

sorption of Cr(VI) onto water hyacinth biochar was influenced by factors like solution pH, adsorbate concentration, adsorbent size, dosage and contact time. The optimum pH for the removal of Cr(VI) was 2.0, biosorbent size= 0.2 mm, biosorbent dosage=2.5 g/100 ml, solute concentration= 100 mg/L of Cr(VI) at 25°C at 250 rpm after 36 hrs. From the data obtained, it is clear that adsorption process follows Langmuir model (monolayer) and kinetics follows a pseudo second order kinetics (chemisorption). Further, the water hyacinth biochar can be utilized for the removal of Cr(VI) from industrial waste water, where there may be competition between different metal ions for adsorption sites onto the adsorbent.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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