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Biosequestration of chromium (VI) from aqueous medium using carbonaceous adsorbents derived from *Eichhornia crassipes*

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Abstract

Utilization of the biochar that are derived from *Eichhornia crassipes* (water hyacinth) as biosorbent for Cr (VI) adsorption was investigated. The biochar was characterized before and after Cr (VI) adsorption by SEM, FTIR and EDX. The influencing parameters *viz.*, solution pH, solute concentrations, reaction duration, adsorbent dose and size have been examined. The most favorable conditions for Cr (VI) removal were found to be pH = 2.0, adsorbent size = 0.2 mm, adsorbent dosage = 2.5g/100ml, adsorbate/solute concentration = 100mg/L of Cr (VI) at 25°C at 250 rpm. Rate of adsorption was rapid and equilibrium was reached at 36 hours. The equilibrium relationship between the sorbent and sorbate was determined using the isotherms Langmuir, Freundlich and Temkin models. The Langmuir dimensionless constant (K_R) for each of the solute concentration was ranged between 0 and 1, it indicates the favourable adsorption of Cr (VI) onto the adsorbent. Adsorption data was very well explained through Langmuir isotherm where sorption occurs on monolayer with the maximum biosorption capacity of 55.55 mg/g. Adsorption rate and its mechanisms were elucidated through kinetic studies *viz.*, Pseudo first order, second order, elovich and intra particle diffusion models. On comparison with various kinetic models, results fitted excellently with pseudo second order model ($R^2=0.999$). It suggests that Cr (VI) adsorption by could be better described by chemisorption which involves sharing of electrons between adsorbents and adsorbate. Hence, the biochar derived from *E. crassipes* are efficiently used as an ecofriendly biosorbent for the management of Cr (VI) rich waste water.

Keywords: Biosequestration, biochar, chromium (VI), adsorbent, isotherm, kinetics

Introduction

Water is a basic human need which is well emphasized by the saying “A single drop of water is more worth than a sack of gold to the thirsty man”. Though it is indispensable commodity, discharge of industrial wastes into them beyond its carrying capacity imparts serious threat to the aquatic ecosystem (Kamaludeen *et al.*, 2003). Heavy metals are one of the trace metals, known to be persistent, toxic, resist biodegradability and originated from variety of industries. Among the heavy metals, Cr is significant obstruction worldwide due to its diverse usages in industries *viz.*, tanning of hides, electroplating, alloying, refractory, textile dyes, metallurgy, paint, chemical manufacturing, petroleum refining etc. (Avudainayagam *et al.*, 2003; Akpor *et al.*, 2014).

Among the industries, tannery industry attained a special attention as it is ranked as one among the red category industry. The major pollutants released from the tanning industry are chromium, chlorides, sulphate, cadmium, sulphites, tannins, organic chemicals in traces and huge quantities of synthetic chemicals (Jahan *et al.*, 2014). With reference to Cr, a part of the Cr salts (60-70%) used in the process of tanning reacts with skin; the remaining quantity (30-40%) in exhaust bath which is directly discharged into sewage without proper treatments. During the foresaid process, it releases enormous quantity of effluent which is rich in chromium. Though many agencies like USEPA (United States Environmental Protection Agency, 1990) and other governmental organizations have stringent norms that maximum permissible limit for Cr (VI) from industrial discharge to surface water (0.1 mg L^{-1}) and potable water (0.05 mg L^{-1}), the existing situation is not in hold polluting the major water bodies of the nation.

Chromium is one among the inorganic transition metal pollutant with a multifaceted electronic as well as valence shell chemistry (-2 to +6) (Shahid *et al.*, 2017). Among the forms, environmentally significant forms are trivalent (Cr (III)) and the hexavalent (Cr(VI)) chromium. These oxidation states of chromium differ in their mobility in addition to its toxicity. Hexavalent chromium is highly mobile, carcinogenic but in case of trivalent chromium Cr(III) is comparatively immobile and less toxic. Chromium (III) plays a major role in metabolism of lipid and sugars furthermore regarded as a key trace element for the well being of human and animal health. Though Cr (III) has beneficial role in metabolism, its uptake in higher quantity will cause health effects. As Cr (III) is less toxic in addition to immobile, but environmental circumstances,

multifaceted physico-chemical and biological factors have the potential to convert it into Cr (VI). As Cr (VI) has higher mobility, it may readily leaches down through soil profile thereby contaminate the groundwater resources (Parameswari *et al.*, 2021).

Considering the Cr toxicity, it is necessary to regulate protect environment and human health. In India about 2000 - 3000 tonnes of chromium from tannery industries were released into the environment per year (Altaf *et al.*, 2008), with the concentration of Cr in the effluent ranged from 2000 to 5000 mg L⁻¹ compared to the maximum permissible limit of 2.0 mg L⁻¹. In this situation, the tannery effluent must be treated properly before discharging into the environment.

For the removal of this toxic pollutant many conventional treatment technologies *viz.*, chemical precipitation, reverse osmosis, electro -dialysis, membrane filtration, and reduction are available (Khatoon *et al.*, 2013) but it's expensive nature, requirements of more energy and generation of huge quantity of toxic sludge requests economically viable and ecologically sound technology. It directs the concentration towards the biosorption process. Biosorption is one among the physico-chemical process where biomass concentrates the pollutant on its surface, binds the contaminant onto cellular structure by adsorption, ion exchange, precipitation, absorption and surface complexation process. For this purpose, a novel biosorbent derived from water hyacinth (*Eichhornia crassipes*) was utilized as the resource base as it is the world's most prominent noxious weed grown under wide range of aquatic environments (Sebastian, 2009). This dreaded aquatic weed poses serious challenge to aquatic inhabitants and is often blamed for its choking nature in water bodies. Hence, this study has been planned to utilize the water hyacinth based biochar as adsorbent for the removal of Cr (VI) from aqueous medium.

Materials and methods

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.

Characterization of biosorbent

The adsorbent morphology was analyzed with SEM (Scanning Electron Microscope) (M/s. FEI- Quanta 20, Czech Republic) at 7.00 kV equipped with the back scattered electron detector. The EDX (Energy Dispersive X-ray spectroscopy) was used to determine the elemental composition of the adsorbent. The Fourier transform infrared (FTIR) spectrometry equipped with ATR accessory (Shimadzu, Japan) at wave number of 4000 to 400 cm^{-1} was used to identify the functional groups present in the adsorbent. The spectra were plotted on transmittance axis onto the biochar.

Point of zero charge (pH_{ZPC})

Point of zero charge was determined using solid addition method (Oladoja and Alice, 2009). The pH of the solution adjusted from 2 to 10 ($\text{pH}_{\text{initial}}$) by taking solution of 0.1M KNO_3 (50ml) with the addition of 0.1N HNO_3 or 0.1N NaOH after that 1g of biochar was added into the solution. The mixture was then manually agitated and permitted to equilibrate up to 48hrs and centrifuged at 5000rpm for 5 minutes and then change in pH of solution (pH_{final}) was measured. The difference between initial pH and final ($\Delta\text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$) was plotted against $\text{pH}_{\text{initial}}$ and the point of intersection gave pH_{ZPC} .

Zeta potential

The surface charge of the biochar was measured through its zeta potential. About 0.5mg of the biochar was added to 20 ml of deionised water and the suspension was shaken at 180 rpm for the period of 2 hours using mechanical shaker. Then the suspension was kept in sonic bath to get the colloids and suspension was filtered through whatman no.42 filter paper. The zeta potential and particle size were analysed from the supernatant and suspension respectively by particle size analyser (Horiba Scientific Nanopartica SZ-100, Japan) (Ucar et al. 2014).

Adsorption experiment

Batch experiments were conducted to study the influence of varied solution pH (1 to 9), adsorbent size (0.2 to 4mm), 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. After shaking, the sample was centrifuged at 8000rpm for 10 minutes and filtered through whatman no.42 filter. The remaining concentration of Cr (VI) was determined by micro plasma atomic emission spectrophotometer (MPAES). The experiments were replicated four times.

The amount of Cr (VI) ions adsorbed onto the biochar at equilibrium (q_e) was calculated using eqn.(1).

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

Where,

C_0 - Initial adsorbate concentration in solution (mg/L)

C_e - Equilibrium adsorbate concentration in solution (mg/L)

V - Adsorbate volume (L)

M - Adsorbent mass (g)

The percent Cr(VI) removal from aqueous solution was determined using eqn.(2)

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

Where,

C_0 - Initial concentration of adsorbate in solution (mg/L)

C_e - Equilibrium concentration of adsorbate in solution (mg/L)

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 eqn. (3)

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

Where,

q_m - Maximum monolayer capacity (mg/g),
 q_e - Metal adsorbed at equilibrium (mg/g)
 C_e - Adsorbate equilibrium concentration of (mg/L)
 K_L - Langmuir adsorption constant (L/mg).

Values of K_L and q_m were obtained from intercept and slope of plot between C_0/q_e Vs C_e (Langmuir 1918). The necessary characteristics of Langmuir isotherm expressed through dimensionless constant separation factor (K_R) and are given by eqn. (4) (Kadirvelu *et al.*, 2001)

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

Where K_L and C_0 has already explained above.

Equation (5) represents Freundlich isotherm equation, which is commonly used for describing adsorption on surface (Dada *et al.* 2012).

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

Where,

K_F - Adsorption capacity constant (mg/g)

n - Intensity of adsorbent

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 $n < 1$) (McKay *et al.* 1980).

Temkin isotherm is used for heterogenous surface energy systems and this isotherm assumes the heat of adsorption which is the point of temperature (Tempkin and Pyzher 1940). Eqn. (6) represents the Temkin adsorption equation as furnished below.

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

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

Where,

R - Universal gas constant (8.314 J/mol/K),

T - Temperature (25°C),

b - Temkin isotherm constant,

A - Temkin isotherm equilibrium binding constant (L/g)

B - constant related to heat of sorption (J/mol).

B and A were obtained from slope and intercept of temkin plot between q_e and $\ln C_e$.

Adsorption kinetics

The adsorption rate 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.

Pseudo first order equation or lagergren rate equation is represented by eqn.(7)

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

Where,

q_e - Amounts adsorbed at equilibrium (mg/g),

q_t - Amounts adsorbed at time t (mg/g),

K_1 - Rate constant of pseudo first order adsorption (1/min)

Value of $\log (q_e - q_t)$ was plotted against t.

K_1 and q_e were determined from the slope and intercept of the plot respectively (Abechi et al. 2011).

The pseudo second order kinetic equation is given by eqn.(8)

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

Where,

K_2 - Rate constant of pseudo second order (g/mg min)

Plot of t/q_t and t gives a linear relationship

Values of q_e and K_2 are obtained from slope and intercept respectively.

The elovich model equation is expressed in eqn. (9)

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

Where,

α - Initial adsorption rate (mg/g min)

$1/\beta$ - Number of sites available for adsorption (mg/g)

Values of β and α were obtained from the slope and intercept of plot q_t and $\ln(t)$

The diffusion mechanism is elucidated by intra particle diffusion model and it is given by eqn. (10) (10)

$$q_t = K_{id}t^{1/2} + C_i \quad \text{—————}$$

Where,

K_{id} - Intra particle diffusion rate constant (mg/g min)

C_i - Constant related to thickness of boundary layer (mg/g)

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

Result and Discussion

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 3.90dSm⁻¹. The cation exchange capacity was high with negative zeta potential which suggests the dominance of the adsorbent surface with negative charges.

Table1. Characteristics of water hyacinth biochar

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

Point of zero charge of 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 denoted as the pH at which the net charge of the biochar is zero, having positively charges as that of negatively charged surface functions (He and Tebo 1998).

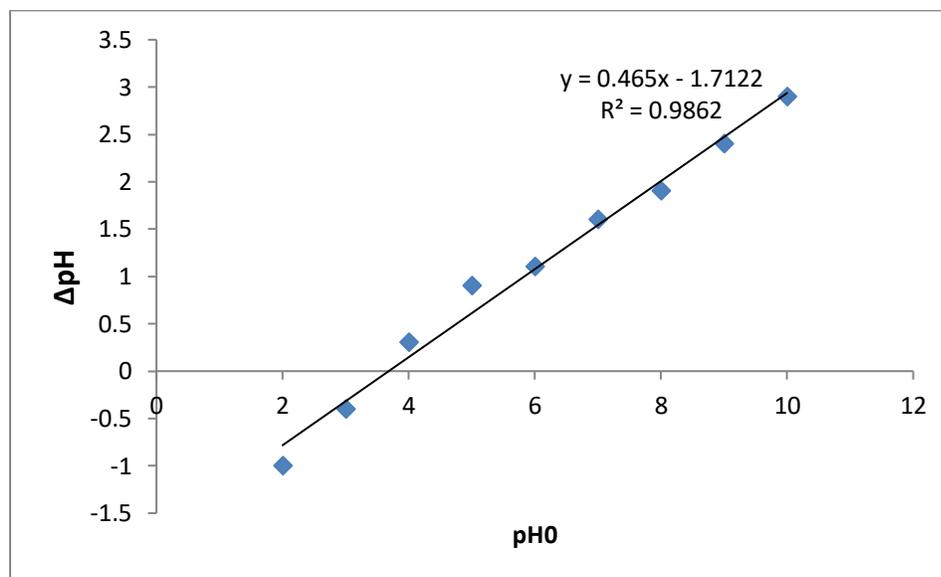


Figure1. Point of Zero charge of water hyacinth biochar

The plot between ΔpH and pH_0 (Fig.1.) shows that the point of zero charge of water hyacinth biochar is 3.7. The adsorbent surface modifies its polarization according to the solution pH (Nascimento et al. 2013). At $\text{pH} > \text{pH}_{\text{ZPC}}$, the adsorbent surface become negatively charged due to the sorption of OH^- by electrostatic attractive force whereas when $\text{pH} < \text{pH}_{\text{ZPC}}$, adsorbent surface attains positive charge due to the adsorption of H^+ (Uddin et al. 2014). Hence, the biosorption of anionic metals (Cr(VI)) will be favoured at $\text{pH} < \text{pH}_{\text{ZPC}}$ (Ebrahimian et al. 2013).

SEM and FTIR analysis of adsorbents

The adsorbent surface morphology was examined by scanning electron microscope (Fig.2).

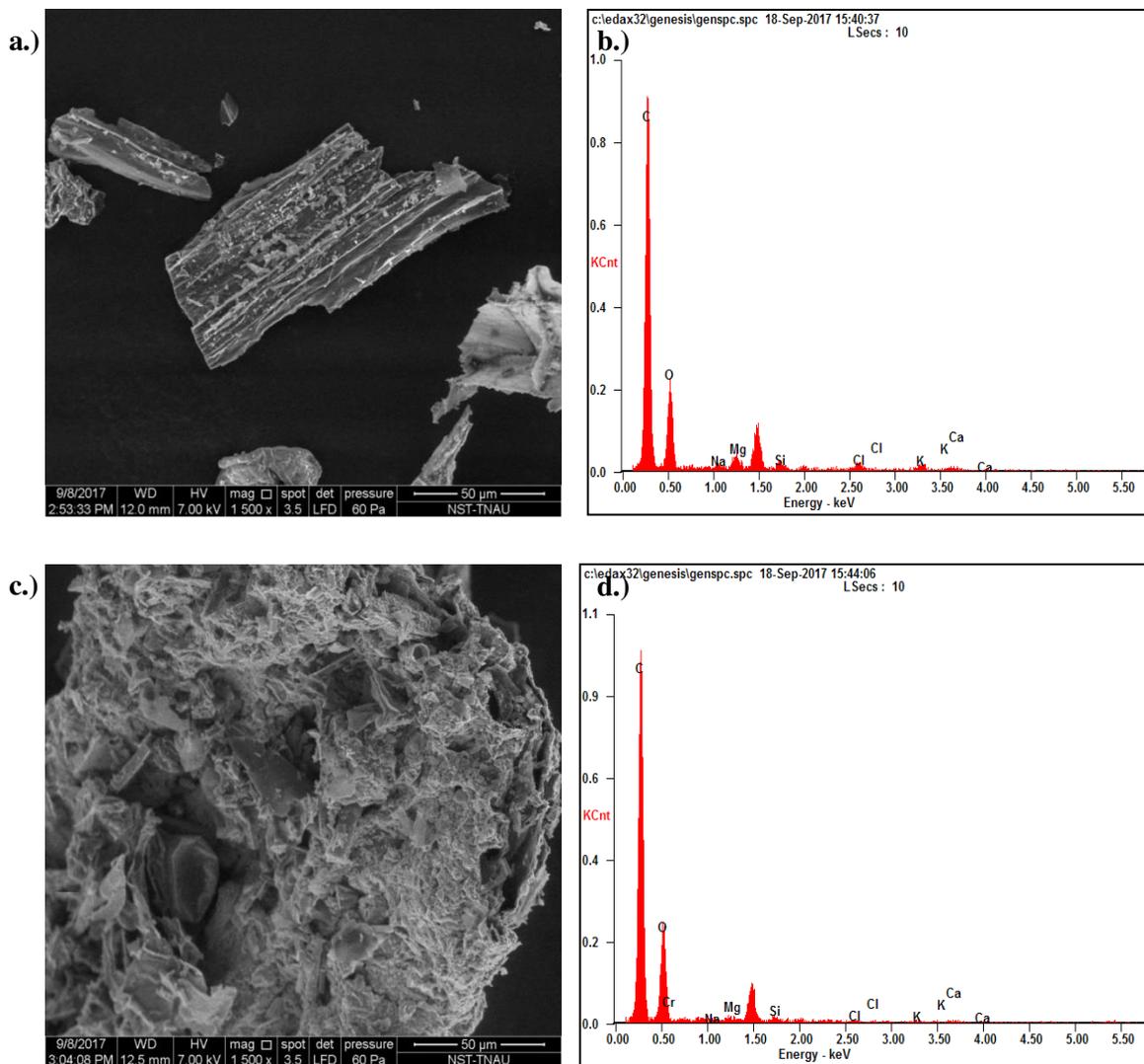
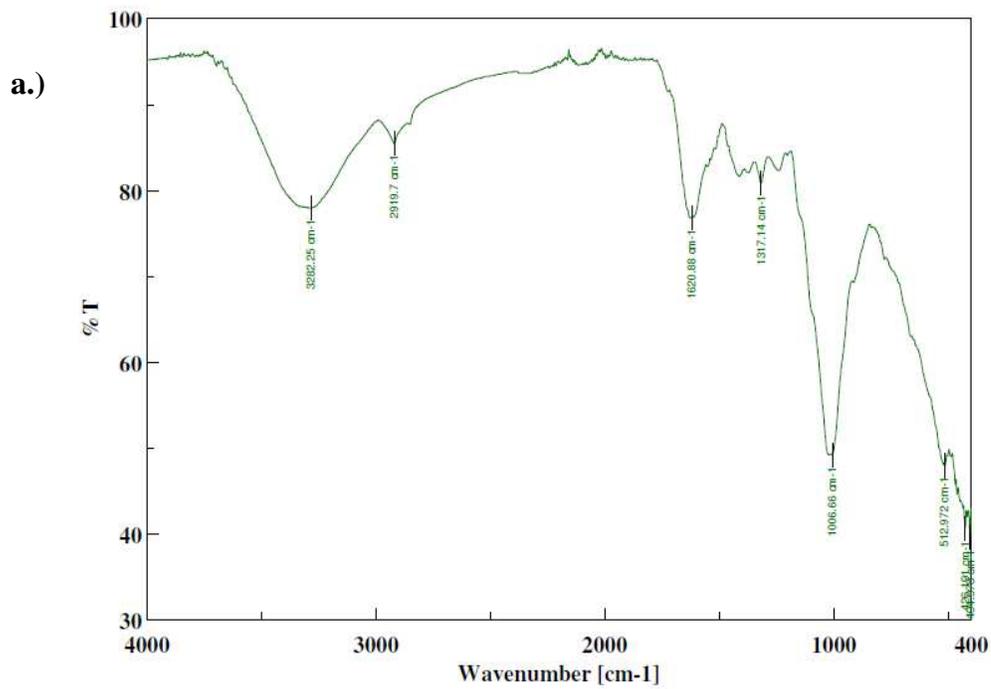


Figure 2. a.) Scanning electron micrographs of water hyacinth biochar, b.) EDX spectra of water hyacinth biochar, c.) Scanning electron micrographs of Cr (VI) loaded biochar, d.) EDX spectra of Cr (VI) loaded biochar

A clear texture of the biosorbent material is depicted in Fig. 2a which provides a large surface for Cr adsorption whereas Fig. 2c depicts a rough aggregated surface. This difference in surface morphology may be attributed by the agglomeration of Cr ions on the adsorbent surface loaded with Cr(VI) (Balarak et al. 2014). The EDX spectra of biochar were given in Fig. 2b & d. The peaks of Ca, O, C indicated the presence of functional groups such as $-OH$ and $-COOH$ in the adsorbent (Jain et al. 2013). 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 (Das and Guha 2007).

The FTIR analysis was conducted with the spectra of the biochar measured in the range of 4000-400 cm^{-1} wavenumber (Fig.3).



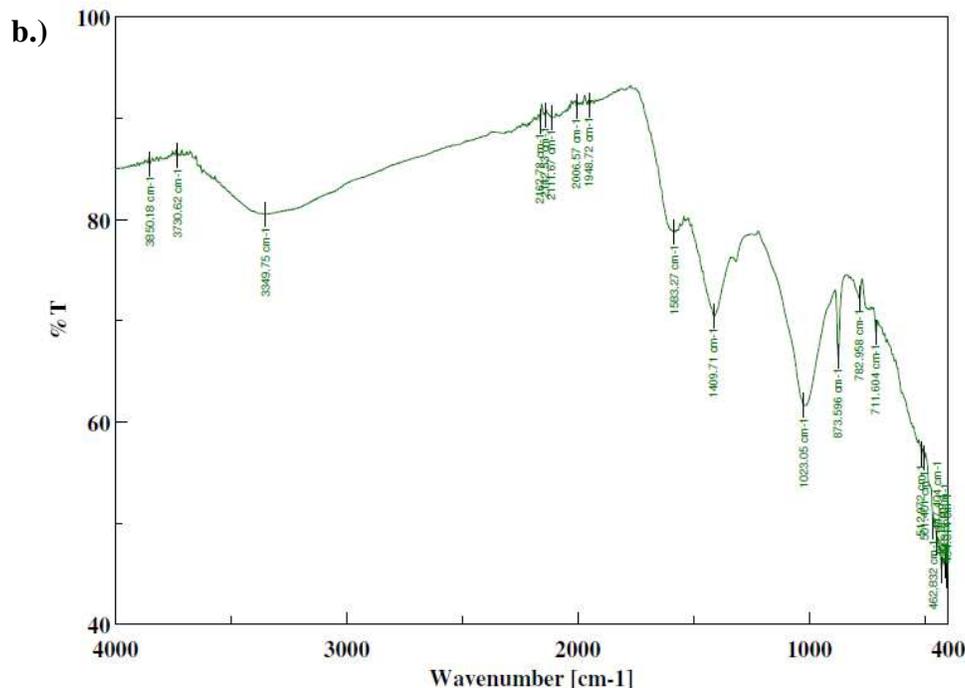


Figure3. FTIR spectra of water hyacinth biochar a.) before Cr adsorption, b.) after Cr (VI) adsorption

Table2 shows the FTIR absorption peaks of native and Cr(VI) loaded biochar which confirmed the existence of numerous functional groups on adsorbent surface. FTIR spectra of biochar before Cr(VI) adsorption showed intense peaks at 3282.25cm^{-1} representing -OH groups which on Cr(VI) loading gets shifted to 3349.75cm^{-1} . The peak at 2919.7 cm^{-1} in biochar might be due to the alkyne group (C-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 1620.88cm^{-1} in unloaded water hyacinth biochar can be assigned to the amine groups. This peak has been shifted to 1583.27cm^{-1} in Cr(VI) loaded biosorbent. The biochar showed strong peak at 1006.66cm^{-1} attributed by C-O groups which gets shifted to 1023.05 cm^{-1} after adsorption of Cr(VI).

Table2. FTIR absorption peaks (cm^{-1}) of native and Cr(VI) loaded WHB

Adsorbent	-OH	C-H	C-O	-NH ₃
WHB	3282.25	2919.7	1006.66	1620.88
WHB loaded with Cr(VI)	3349.75	-	1023.05	1583.27

*WHB- Water Hyacinth Biochar

From the FTIR spectral data, it is clear that -OH , C-H , -NH_3 , C-O 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 metal binding.

Effect of pH on Cr(VI) adsorption

The pH, solute concentration, adsorbent size, dosage and contact time are known to be the factors affecting adsorption of adsorbate. 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 (Bedemo et al. 2016). The maximum adsorption of Cr(VI) at pH 2.0 might be due to the fact that at lower pH the adsorbent surface acquires a positive charge which can easily bind negatively charged Cr(VI) through electrostatic force of attraction (Tarley & Arruda 2004; Mohanty et al. 2006).

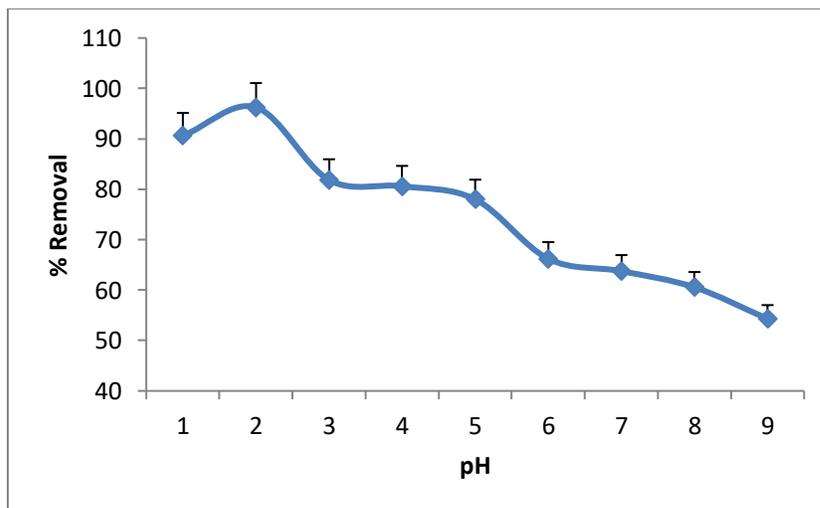


Figure4. Effect of solution pH on Cr(VI) adsorption

Effect of adsorbent size on Cr(VI) adsorption

To analyze the effect of adsorbent size in adsorption process, series of experiments were carried out at fixed solute concentration of 200 mg/L of 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, 0.2mm recorded the maximum removal of Cr(VI) (96.55%) followed by 0.5 mm (95.15%). Higher adsorption by smaller size of the adsorbent was due to the decrease in particle size increases the surface area and more number of binding sites for adsorption increases with increases in surface area (Muthulakshmi and Anuradha 2015).

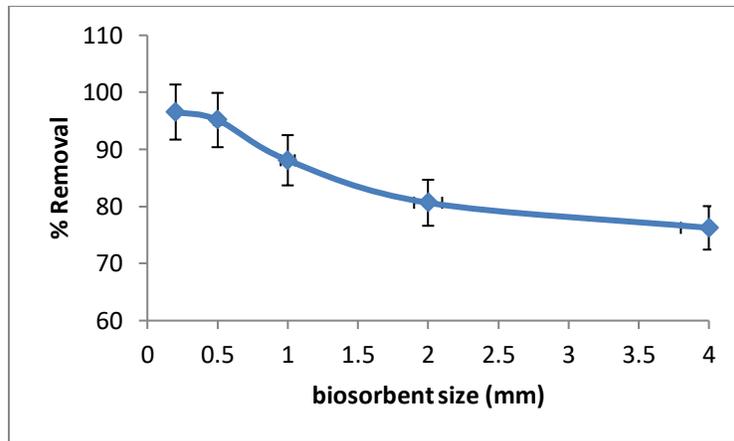


Figure5. Effect of adsorbent size on Cr(VI) adsorption

Effect of adsorbent dosage on Cr(VI) adsorption

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 (Mohammed et al. 2013).

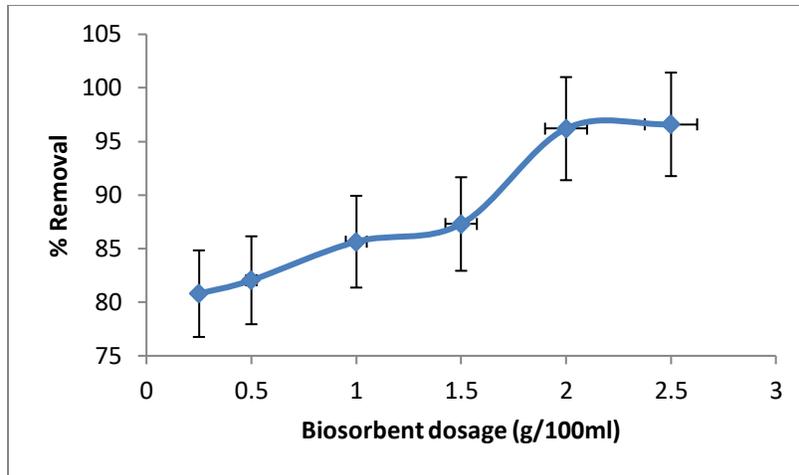


Figure6. Effect of biosorbent dosage on Cr(VI) adsorption

Effect of solute concentration on Cr(VI) adsorption

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 (Martinez et al. 2006; Freitas et al. 2008).

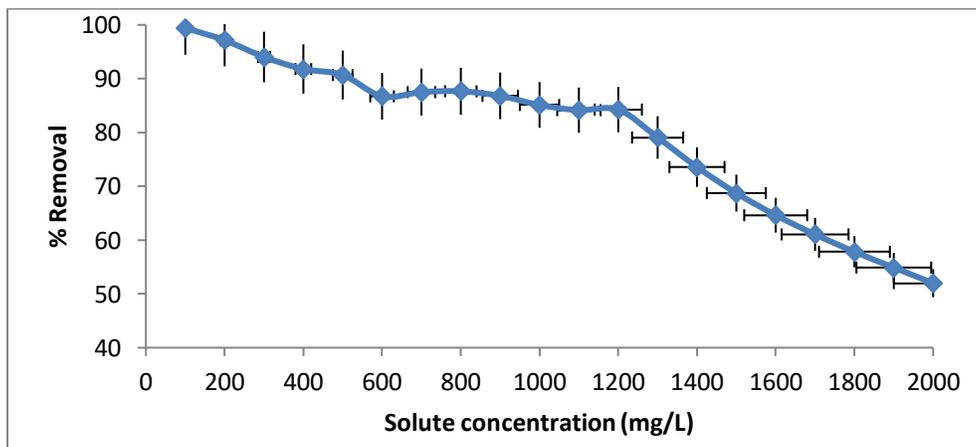
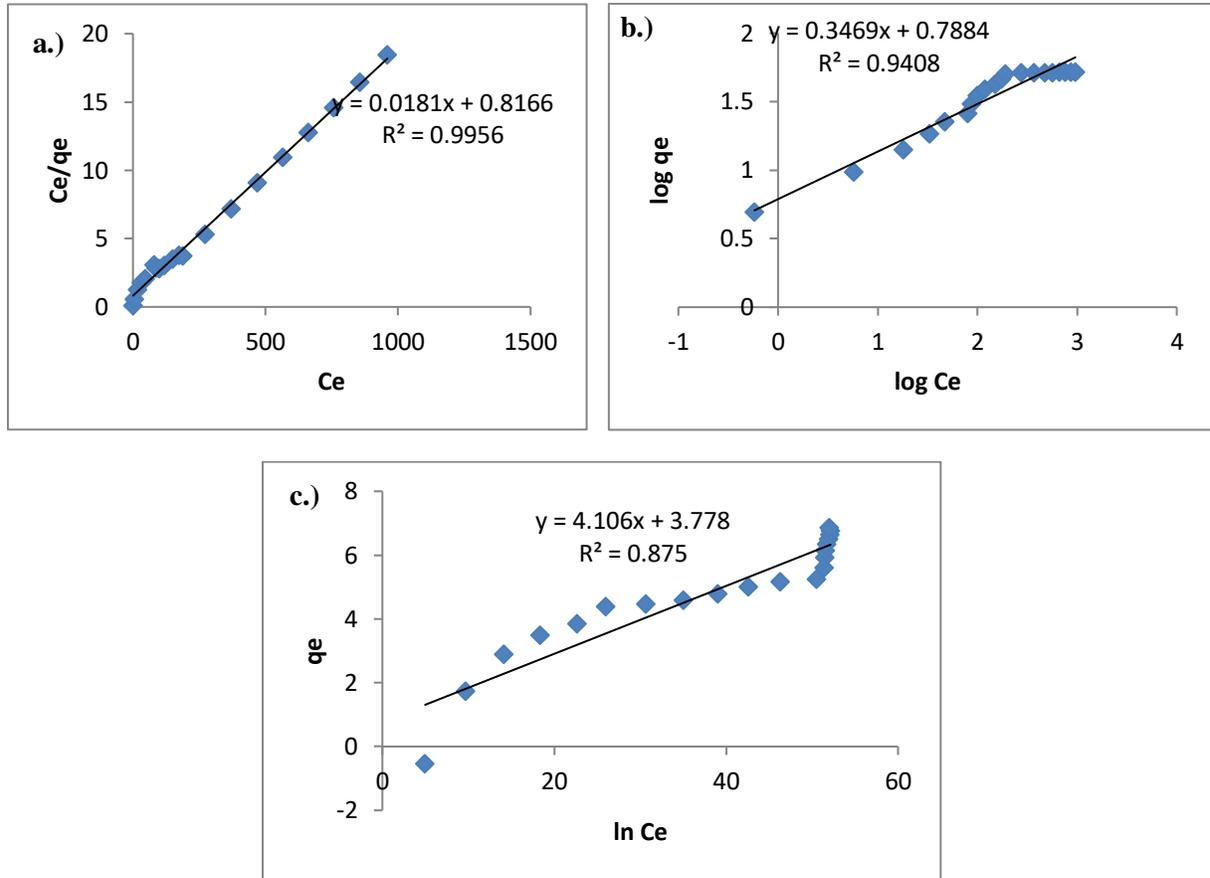


Figure7. Effect of solute concentration on Cr(VI) adsorption

Isotherm study

The data obtained from the batch experiment to study the effect of solute concentration were fitted to isotherms like Langmuir, Freundlich and Temkin.



**Figure8. Isotherm plots for adsorption of Cr (VI) onto water hyacinth biochar
a.) Langmuir isotherm, b.) Freundlich isotherm, c.) Temkin isotherm**

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 Table3. 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, this being the case for water hyacinth biochar studied presently (Table 3). Higher R^2 value of 0.999 was obtained for Langmuir isotherm model, which confirmed that adsorption of Cr(VI) onto biosorbent occurred onto the active sites as monolayer (Adbel- Aty et al. 2013).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 Table5. 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.

Table3. Isotherm constants for adsorption of Cr (VI) to water hyacinth biochar

Constants	
Langmuir isotherm	
q_m (mg/g)	55.55
K_L (L/mg)	0.022
R^2	0.995
Freundlich isotherm	
n (L/mg)	2.89
K_F (mg/g)	6.14
R^2	0.940
Temkin isotherm	
B	4.16
A (L/g)	2.51
R^2	0.875

Table4. 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

Table5. Cr(VI) adsorption capacity of different adsorbents

Adsorbent	Adsorption capacity (mg/g)	Reference
Banana peel	131.56	Memon et al. 2009
Groundnut hull (modified)	131.00	Owalude et al. 2016
Cyanobacteria biomass	103.09	Das 2012
Biomass of <i>Canna indica</i>	71.43 (at temperature 30°C)	Dixit et al. 2014
Saw dust activated carbon	65.80	Karthikeyan et al. 2005
Leaves of <i>Melaleuca diosmifolia</i>	62.50	Saranya et al. 2016
Treated newspaper	59.88	Dehghani et al. 2016
Water hyacinth biochar	55.5	This study
Sunflower stem waste	47.3	Jain et al. 2010
Rice husk carbon	45.6	Srinivasan et al. 1988
Coconut husk fibre carbon	29.0	Huang & Wu, 1977
Activated carbon from <i>Syzygium jambolanum</i> nut	27.2	Muthukumaran & Beulah, 2011
Sugarbeet pulp carbon	24.20	Aitundogan et al. 2007
Coconut shell carbon	20.0	Alaerts et al. 1989
Mango kernel activated carbon	7.80	Rai et al. 2016
Potato peelings	3.28	Mutongo et al. 2014
Silica sand coated with groundwater treatment residuals	0.27	Kan et al. 2017

Effect of contact time on Cr(VI) adsorption

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 major adsorption of Cr(VI) (81.60%) occurred at 6 hrs and at equilibrium 97.4% of Cr(VI) was removed. The initial rapid adsorption might be due to large number of active sites available for adsorption (Leon et al. 2017) 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 (Alslaibi et al. 2014).

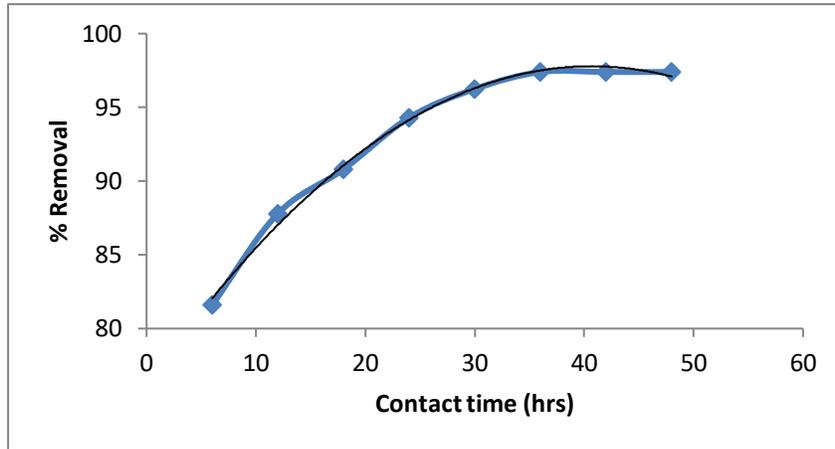
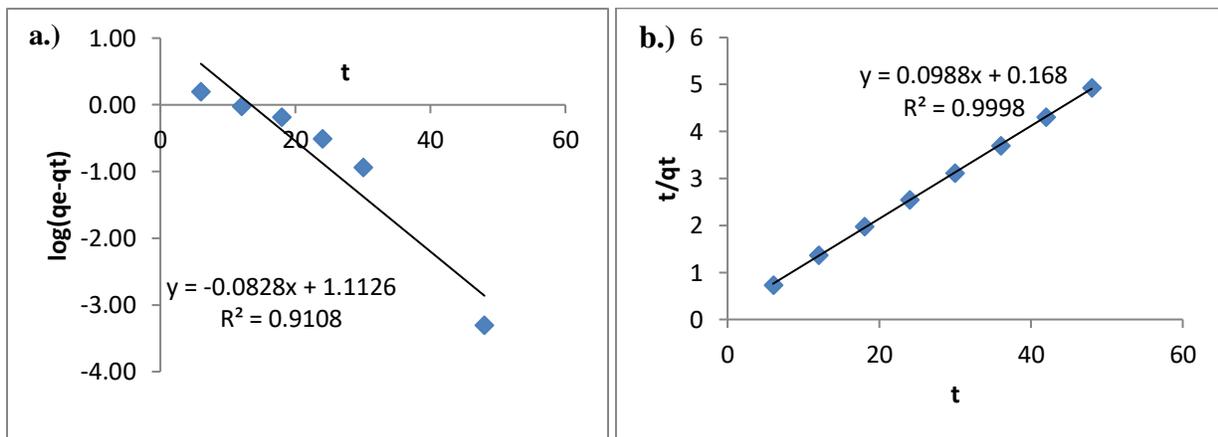


Figure9. Effect of contact time on Cr(VI) adsorption

Kinetic study

The rate of adsorption and its mechanisms were elucidated through kinetic studies.



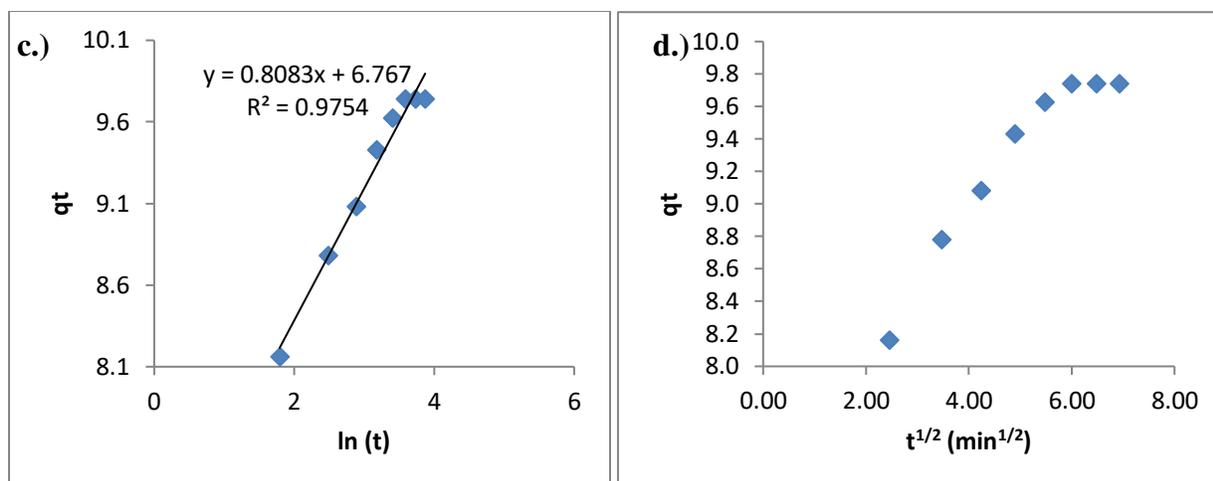


Figure10. Kinetic plots for adsorption of Cr (VI) onto water hyacinth biochar a.) Pseudo first order kinetic model, b.) Pseudo second order kinetic model, c.) Elovich model and d.) Intraparticle diffusion model

The data obtained from the adsorption kinetic study were furnished in Table 6. According to Table 6, 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 (Bernard and Jemoh 2013) which involves sharing of electrons between adsorbents and adsorbate (Deng et al. 2009). To obtain valid information pertaining to process involved in the adsorption mechanism, the data were further examined by intra particle diffusion model. The multi linear plots were obtained from diffusion model which shows that two or more steps were involved in the sorption process (El-Said 2010). From the plots of intra particle diffusion model depicted in fig. 10.d, it was evident that adsorption process had two steps. 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 (Adbel-Ghani et al. 2015; Premalatha et al. 2019).

Table6. Kinetics constants for adsorption of Cr (VI) to water hyacinth biochar

Constants	Values
Pseudo first order model	
(q _e) _{exp} (mg/g)	9.740
(q _e) _{cal} (mg/g)	12.94
K ₁ (min ⁻¹)	0.189
R ²	0.910
Pseudo Second order model	
(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
Elovich model	
α (mg/g min)	3.504X 10 ³
β (g/mg)	1.238
R ²	0.975
Intraparticle diffusion model	
Ki (mg/g min)	0.358
C	7.494

Conclusion

This study shows that biochar derived from water hyacinth effectively adsorbs Cr(VI) from aqueous solution. Therefore, after the adsorption of Cr (VI) the biosorbent may be regenerated with mineral acids through desorption process. The rejuvenated biosorbents again utilized for adsorption cycles in addition chromium recovered from biosorbent may be utilized effectively for leather tanning purpose. It will considerably reduce the process cost in the leather industry. From this study it is evident that water hyacinth based bio sorbent will act as an ecofriendly bio system for the management of Chromium pollution in the environment while considering the economic aspects of wastewater treatment. Hence, this pilot scale technology may be upgraded in to larger scale in the industries.

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