

Adsorption of Trivalent Chromium on Biochar Derived from Aquatic Weed Biomass

Premalatha R. P., Sowndarrajan P. T., Parameswari E., Malarvizhi P.

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ABSTRACT

The chromium ion released from multifarious industries made the water resources unfit for the life supporting activities. In this study, biochar prepared from the aquatic weed water hyacinth was tested for the adsorption of Cr (III) from aqueous solution at different solution pH (1 to 9), initial Cr (III) concentration (100 to 2000 mg L⁻¹) and contact time (6 to 48 hrs). The study revealed that more than 90% of Cr (III) adsorption took place at pH of 4.0 with contact time of 12 hrs. The adsorption data fitted well with Langmuir isotherm (monolayer adsorption of Cr (III)

onto adsorbent) and pseudo second order kinetics (chemisorption). The maximum Cr (III) adsorption capacity (q_m) of 41.7 mg g⁻¹ was observed. This can be better utilized for the removal of chromium ions from tannery effluent.

Keywords Adsorption, Biochar, Trivalent chromium, Isotherm Kinetics.

INTRODUCTION

Urbanization and industrialization had increased pressure on the water bodies and made the precious resource unfit not only for drinking but also for other life supporting activities. The water sources are contaminated by wide range of contaminants, among which the heavy metals drawn special attention because of their toxic and non biodegradable nature. From this category, chromium is utilized in the industrial processes such as alloying, electroplating, metal finishing, metallurgy, leather manufacture, textile dyes, refractory, paint, chemical manufacturing and petroleum refining etc (Nur-E-Alam *et al.* 2020, Avudainayagam *et al.* 2003). India is the largest exporter of leather products but tanneries were classified under red category by Ministry of Environment and Forests, Government of India. Though different tanning methods were available to make leather, about 85-90% of the leathers were obtained through chrome tanning (Sundar *et al.* 2002, Gustavson 1956) because of its faster leather production techniques, higher hydrothermal stability and extraordinary leather qualities (Mengistie *et al.* 2016). Approximately 60-70% of the added chromium is

Premalatha RP ^{1*}

¹PhD Scholar

Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, India

Present Affiliation: ¹Scientist, ICAR - Indian Institute of Oil Pal Research, Pedavegi 534450, Andhra Pradesh, India.

Sowndarrajan PT²

Assistant Professor, School of Advanced Sciences, Vellore Institute of Technology, Chennai 600127, Tamil Nadu, India

Parameswari E³

Assistant Professor, Department of Environmental Sciences, Tamil Nadu Agricultural University, Coimbatore, India

Malarvizhi P⁴

Professor, Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University, Coimbatore, India

Email: premayunani@gmail.com

*Corresponding author

diffused into the skin and about 30-40% remains in wastewaters (Sivakumar *et al.* 2008, Cassano *et al.* 2007). Apart from this, post tanning operations like washing, acidification, rechroming and neutralization also releases considerable quantities of chromium. A total of around 60% of chromium salts added in the tanning process is released in wastewater (Zhou *et al.* 2012). Conventional and high exhaust chrome tanning results in wastewater containing 1500 to 3000 and 500 to 100 mg of chromium per litre of wastewater (Aravindhnan *et al.* 2004).

There were many treatment technologies to improve the diffusion of chromium and to reduce the quantity of tanning agents like chrome tanning assisted by ultrasound (Mengistie *et al.* 2016), microwave (Zhang and Chen 2020), CO₂ intensified tanning (Prokein *et al.* 2020), etc. Membrane technologies (reverse osmosis, membrane filtration), ion exchange, electrocoagulation, chemical coagulation, and electrodialysis are some treatment techniques for removing chromium from wastewater. However, these techniques have drawbacks like high cost, high reagent and energy requirements, sludge generation, and sometimes poor removal potential at lower metal concentration (1-100 mg L⁻¹) (Nur-E-Alam *et al.* 2020; Song *et al.* 2004, Tiravanti *et al.* 1997). Chromium, an inorganic metal pollutant exists in variable oxidation states (0-VI). The trivalent (Cr (III)) and hexavalent (Cr (VI)) are stable forms of Cr (Bhattacharya *et al.* 2019), which differs from each other in mobility and toxicity. Cr (III) is immobile and non-toxic, whereas the Cr (VI) is highly mobile, toxic with mutagenic, cytotoxic and carcinogenic effects. Though chromium sulfate, trivalent chromium salt is used in tanning process, the interconversion between trivalent and hexavalent forms causes potential environmental risk (Liang *et al.* 2021). It has been reported that tannery effluent contains hexavalent chromium of 0.33 to 3.46 mg L⁻¹ (Mahmood *et al.* 2013).

Considering this, there arises a need of environmentally safe and economically technology to treat heavy metals from industrial wastewater. Phytoremediation of heavy metals through hyperaccumulators is an environmentally safe option but the short lived and slow growth nature of hyperaccumulating plants limits the efficiency of phytoremediation (Yan *et al.*

2020). Biosorption is proved to be an effective method in heavy metal removal (Volesky 2003, Kratochvil and Volesky 1998) at lower cost utilizing crop residues, weeds, microbial biomass (algae, bacteria, fungi, actinomycetes) as biosorbents. The advantages of biosorption over conventional treatment techniques are low cost, eco-friendly, higher efficiencies at low metal concentrations, higher metal binding capacity, and reusability after metal recovery (El-Naggar *et al.* 2018). Boota *et al.* (2009) reported a reduction in metal adsorption by adsorbent (lignocellulosic fiber from Citrus reticulate biomass) at higher dosage due to the aggregation of adsorbents. Water hyacinth (*Eichhornia crassipes*) is a rapid growing floating aquatic weed which destroyed many water bodies and are difficult to manage (Honlah *et al.* 2019). With the higher biomass yield of 100 to 120 t ha⁻¹ yr⁻¹, conversion of water hyacinth biomass to biochar is found to be sustainable option to manage this weed (Masto *et al.* 2013). Biochar has the carbon, which is recalcitrant and resistant to microbial attack (Woolf *et al.* 2010). It is an environmentally friendly material with the properties similar to the activated carbon. Considering its greater availability in the study area, water hyacinth biochar (WHB) was utilized as an adsorbent in this study. The objectives of this study were 1) to determine optimum conditions for Cr (III) adsorption from aqueous solution, 2) to study the adsorption isotherm and kinetics of Cr (III) adsorption onto WHB.

MATERIALS AND METHODS

Adsorbent preparation

Water hyacinth plants were collected from Vaigai dam (77°35'23"E and 10°03'12"N), Theni district, Tamil Nadu, India. The aquaphytes were washed to remove sediments and other small floating fresh water aquatic weeds like *Lemna minor* and dried under sunlight. The biochar is prepared from water hyacinth plants through pyrolysis (at 450°C for 2-3 hours) and pulverized with a blender, sieved through 0.2 mm sieve and stored in air tight containers for further analysis.

Adsorbate

Analytical reagent grade chemicals were used in this

experiment. The stock solution of Cr (III) (2000 mg L⁻¹) was prepared by dissolving their sulphate salt (Cr₂(SO₄)₃·H₂O). Appropriate dilution of the above stock was done to obtain the required concentration further.

Characterization of adsorbent

The pH and EC of WHB was determined with adsorbent: water ratio of 1:25 using the pH meter and conductivity bridge respectively. The scanning electron microscopy (M/s. FEI- Quanta 250, Czech Republic at 7.00 kV equipped with the back scattered electron detector) was carried out to analyze the surface morphology of WHB before and after Cr (III) adsorption. Energy dispersive X-ray analysis (EDAX) was used to determine the elemental composition of the adsorbent sample. The infrared spectra was obtained through fourier transform infrared (FTIR) spectrometry equipped with a diamond tipped ATR accessory (Shimadzu, Japan) at wave number of 4000 to 400cm⁻¹ (8400 S of Shimadzu, Japan) to identify the functional groups associated with WHB and chemical changes on Cr (III) adsorption. BET (Brunauer – Emmett- Teller) surface area of WHB was determined using BET surface analyser (Smartsorb 92/93). The zeta potential of WHB was determined by particle size analyzer (Horiba Scientific Nanopartica SZ-100, Japan).

Solid addition method was used to determine zero point charge (ZPC) (Oladoja *et al.* 2009; Balisrieri *et al.* 1982). This experiment was carried out by taking solution of 0.1M KNO₃ (50 ml) with their pH adjusted from 2 to 10 (pH_{initial}) by adding 0.1N HNO₃ or 0.1N NaOH and then 1.0 g of WHB was added. The mixture was then manually agitated and allowed to equilibrate for 48hrs and centrifuged at 5000 rpm for 5 minutes and then change in pH of solution (pH_{final}) was measured. The difference in the pH ($\Delta \text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{final}}$) was plotted against pH_{initial} and the point of intersection gave pH_{ZPC}.

Adsorption experiments

Batch studies were carried out at 25±2°C with 100 ml of varying Cr (III) concentration (100 to 2000 mg L⁻¹) at definite time intervals (6, 12, 18, 24, 30, 36, 42 and 48 hrs) using 2.0 g of WHB. The suspension was

continuously agitated by orbital shaker at 250 rpm. Adsorption isotherms were derived for different Cr (III) concentration ranging between 100 and 2000 mg L⁻¹ and kinetics studies were performed. The isotherm and kinetic models for adsorption study are detailed in Table 1. The samples were centrifuged at 8000 rpm for 10 minutes and filtered subsequently. The Cr was quantified using Atomic Absorption Spectrophotometer (Perkin Elmer AA400) at 358 nm with acetylene gas support. Adsorption studies were also conducted to study the effect of solution pH on Cr (III) adsorption with the initial Cr (III) concentration and WHB dosage of 200 mg L⁻¹ and 2g, respectively. The volume of the Cr (III) solution used was 100 ml and the pH range taken for the study was 1 to 9. The pH of the solution was adjusted using 1N NaOH and 1N HCl.

The adsorption capacity of WHB was calculated using equation (1)

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

where q_e : amount of Cr (III) adsorbed per gram of WHB at equilibrium (mg g⁻¹), V : volume of Cr (III) solution taken (L) and M : mass of WHB (g) dispersed in solution, C_o and C_e : initial and equilibrium concentration of Cr(III) solution (mg L⁻¹).

The percent adsorption of Cr (III) from aqueous solution was determined using equation (2)

$$\% \text{ adsorption} = \frac{(C_o - C_e)}{C_o} \times 100$$

RESULTS AND DISCUSSION

Characterization of adsorbents

The per cent recovery of the WHB from the biomass was found to be 21.5 % which is lower than coconut shell carbon (Piriya *et al.* 2020). The WHB was found to be alkaline (9.83) with electrical conductivity of 3.90dSm⁻¹. Enhancement of oxides, carbonates, and hydroxides on pyrolysis resulted in higher pH (Domingues *et al.* 2017). The negative zeta potential (-21.3 mV) indicated the predominance of the negative charges on the adsorbent surface. It was due

Table 1. Isotherm and kinetic models for adsorption study.

Model	Formula	Parameters	References
Adsorption isotherms			
	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ $K_R = \frac{1}{1 + K_L C_0}$	q_m : maximum monolayer coverage capacity (mg g^{-1}), q_e : amount of Cr adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), C_e : concentration of Cr at equilibrium (mg L^{-1}) K_L : constant representing the affinity of active binding sites (L mg^{-1}) K_R : Dimensionless constant separation factor	Langmuir 1918
Freundlich	$q_e = K_f C_e^{1/n}$	K_f : constant related to adsorption capacity (mg g^{-1}), n : intensity of adsorbent	Foo and Hameed 2010
Temkin	$q_e = \frac{RT}{B} \ln A + \frac{RT}{b} \ln C_e$	R : universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$), T : temperature (25°C), b : Temkin isotherm constant, A : Temkin isotherm equilibrium binding constant (L g^{-1}) B : constant related to heat of sorption (J mol^{-1}).	Temkin and Pyzhev 1940
Adsorption kinetics			
Pseudo first order	$\log (q_e + q_t) = \log q_e - \frac{K_1}{2.303} t$	q_e and q_t : amounts adsorbed at equilibrium and at time t (mg g^{-1}), K_1 is the rate constant of pseudo first order adsorption (min^{-1})	Lagergren 1898
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	K_2 : rate constant of pseudo second order rate equation ($\text{g mg}^{-1}\text{min}^{-1}$)	Ho <i>et al.</i> 2002
Elovich	$q_t = \left(\frac{1}{\beta}\right) \ln (\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$	α : initial adsorption rate ($\text{mg g}^{-1}\text{min}^{-1}$) $1/\beta$: number of sites available for adsorption (mg g^{-1})	Zafar <i>et al.</i> 2019
Intra particle diffusion model	$q_t = K_{id} t^{1/2} + C_i$	K_{id} : intra particle diffusion rate constant ($\text{mg g}^{-1} \text{min}^{-1}$) C_i : constant related to thickness of boundary layer (mg g^{-1})	Weber and Morris 1963

to the predominance of anionic functional groups (Mozammel *et al.* 2002). The BET surface area was found to be $216 \text{ m}^2 \text{ g}^{-1}$.

Surface morphology

SEM micrographs and EDAX spectra of WHB before and after Cr (III) adsorption are depicted in Fig. 1. There is a clear striated and nebulous texture of untreated WHB which may provide large surface for the adsorption of Cr. However, after Cr (III) adsorption,

the surface morphology has been changed to rough aggregated and irregular microstructures. This difference in surface morphology authenticates the adsorption of Cr (III) onto WHB. The EDAX spectra were also recorded to know the elemental composition of WHB before and after Cr (III) adsorption. The peaks of calcium, oxygen and carbon indicated the existence of functional groups like $-\text{OH}$ and $-\text{COOH}$ in WHB (Jain *et al.* 2013). The EDAX spectra of WHB before Cr adsorption showed no prominent peaks of chromium whereas the spectra after Cr (III) adsorption

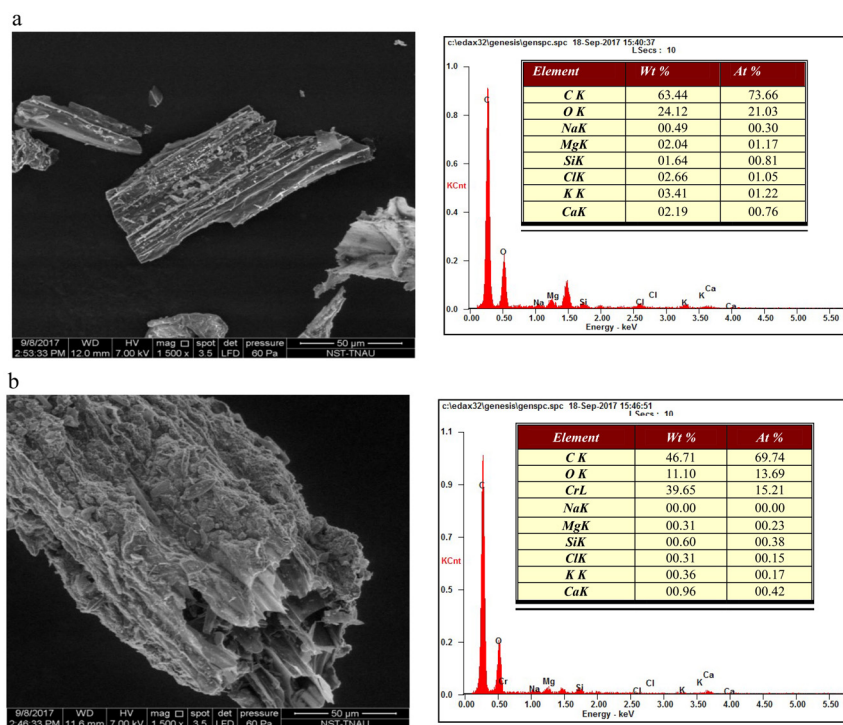


Fig. 1. Surface morphology and EDAX spectra of WHB a.) before, b.) after Cr (III) adsorption.

produced prominent chromium peaks with the reduction in calcium peaks (Das *et al.* 2007). Similar trend of reduction in composition of magnesium, sodium, potassium, chloride is also observed.

Functional properties

FTIR spectra provide information on the functional groups present in WHB before and after Cr (III) adsorption as shown in Fig. 2. The spectra observed between 3321 and 1408 cm^{-1} correspond to the OH groups and C-H deformations of lignin, respectively (Alemu *et al.* 2019, Shahadat *et al.* 2015). The narrow and broad spectra between 1500 - 1600 cm^{-1} was due to C-C vibrations and presence of phosphorus in bio-char, respectively (Piriya *et al.* 2020). C-O stretching appeared between 1219 - 1381 cm^{-1} (Shahadat *et al.* 2015). The spectra at 2319 and 2321 cm^{-1} attributed to C=C bonds (Lazim *et al.* 2015). The spectra observed between 400 - 500 cm^{-1} correspond to vibrations of Si-O (Saikia *et al.* 2003). The spectra obtained for WHB showed distinct changes after Cr (III) adsorp-

tion. The chemical shift in the positions of functional groups indicated their involvement in the adsorption of Cr (III) onto surface of WHB.

Adsorption studies

pH and pHZPC

The adsorbent characteristics and the level of ionization of metal ions in aqueous solution depend on pH of the solution. The pH range of 1 to 9 was studied for the adsorption of Cr (III) onto WHB. In aqueous solution, trivalent Cr (Cr (III)) present as a cation (Bedemo *et al.* 2016). The lower adsorption of Cr (III) at very low pH was reported due to the competition of H^+ and metal ions (Banat *et al.* 2003) and electrostatic repulsion (Jeon and Holl 2003). The maximum Cr (III) adsorption was observed at pH 4.0 (Fig. 3a), beyond that adsorption of Cr (III) decreased due to metal hydroxide formation at higher pH (Alemu *et al.* 2019, Shahadat *et al.* 2015). The pH of 5.0 showed maximum adsorption of Cr (III) using activated car-

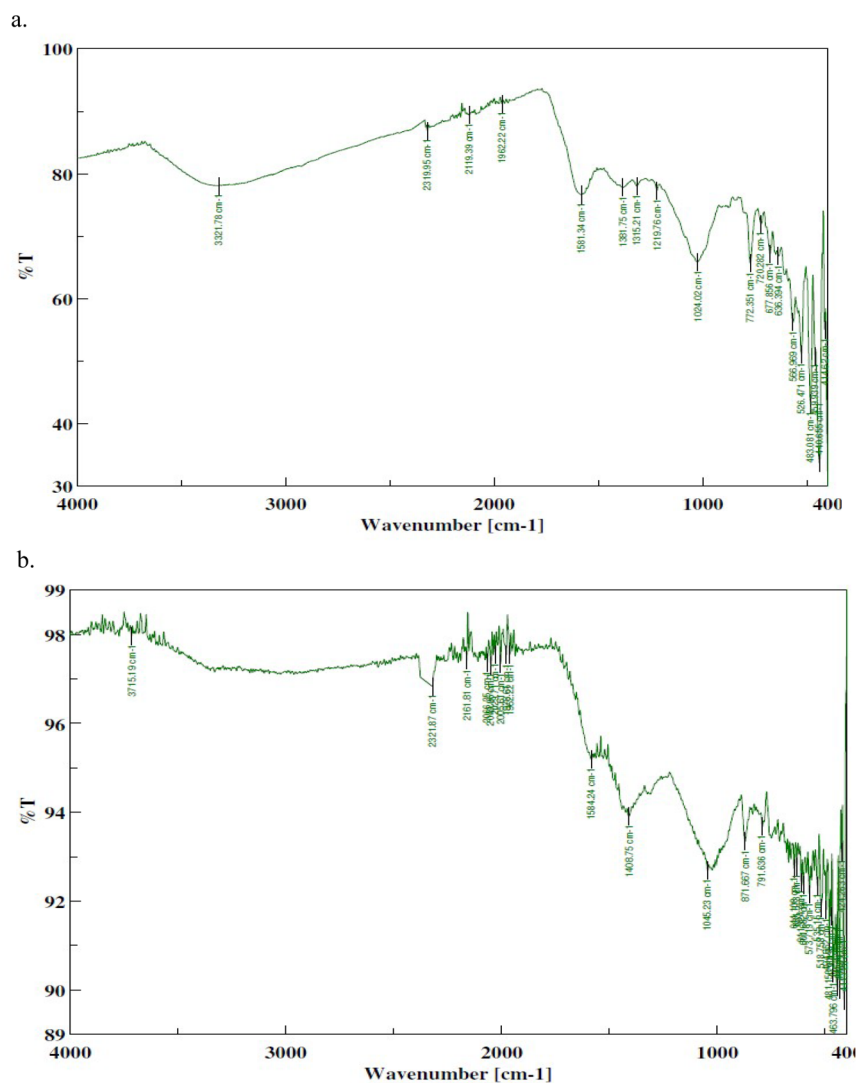


Fig. 2. FTIR spectra of WHB a.) before, b.) after Cr (III) adsorption.

bon of mineral origin as adsorbent (Leyva-Ramos *et al.* 1995). The sorption of metal ions depends on

surface chemistry of the adsorbents where the zero point charge is a useful parameter. The plot between

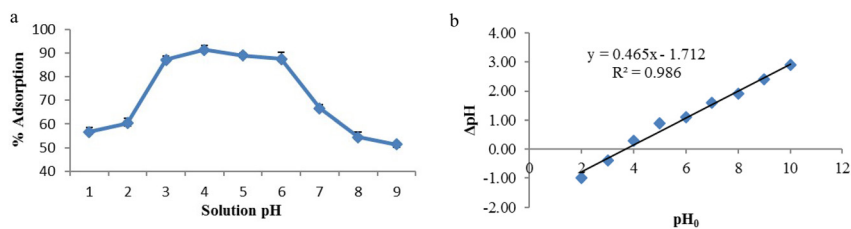


Fig. 3. (a) Effect of solution pH on Cr (III) adsorption, (b) Zero Point charge (ZPC) of WHC.

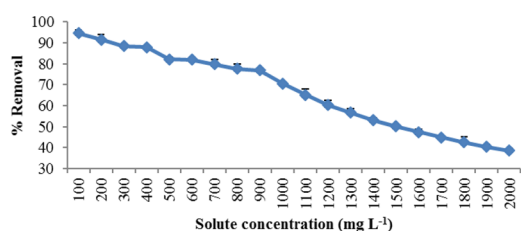


Fig. 4. Effect of solute concentration on per cent removal of Cr (III).

ΔpH and pH_0 shows that the point of zero charge of biochar was 3.7 (Fig. 3b). At $\text{pH} > \text{pH}_{\text{ZPC}}$, the surface of the adsorbent become negatively charged which favours the adsorption of Cr(III) (Sheng *et al.* 2012).

Adsorption isotherms

The maximum % adsorption of Cr (III) recorded at 100 mg L^{-1} solute concentration beyond which the metal adsorption went down (Fig. 4). On increasing the metal concentration, the sorption capacity increased but decreased the removal percent, which might be due to the lack of active binding sites required at higher solute concentration of aqueous solution (Freitas *et al.* 2008, Martinez *et al.* 2006). To understand the adsorption mechanism at solid liquid interface, models like Langmuir, freundlich

and temkin isotherm models were used in the present work. The isotherm plots for Cr (III) adsorption onto WHB are shown in Fig. 5 and the parameters of isotherm models are tabulated in Table 2. The maximum R^2 value was obtained in langmuir isotherm which confirmed that adsorption of Cr (III) onto WHB occurred onto the active sites as monolayer (Abdel-Aty *et al.* 2013). The maximum monolayer adsorption capacity (q_m) of 41.7 mg g^{-1} was recorded. The langmuir dimensionless constant (K_R) for each of the solute concentration was found to be between 0 and 1, which indicated a favourable adsorption of Cr (III) onto WHB (Kadirvelu *et al.* 2001). Considering the freundlich isotherm, the R_2 value was less compared to langmuir isotherm and the 'n' value was in the range of 2-3 indicating favourable adsorption (Mckay *et al.* 1980).

Adsorption kinetics

The mechanism of Cr (III) adsorbed on WHB surface with the contact time (6hrs to 48hrs) and Cr (III) concentration of 200 mg L^{-1} was studied with kinetic models like pseudo first order, second order, elovich and intra particle diffusion (Fig. 6). For adsorption of Cr (III), the equilibrium was attained at 12hrs (Fig. 7) which differs non-significantly with 18, 24, 36, 42 and 48 hrs. The gradation in amount of Cr (III) adsorbed at initial periods was due to the

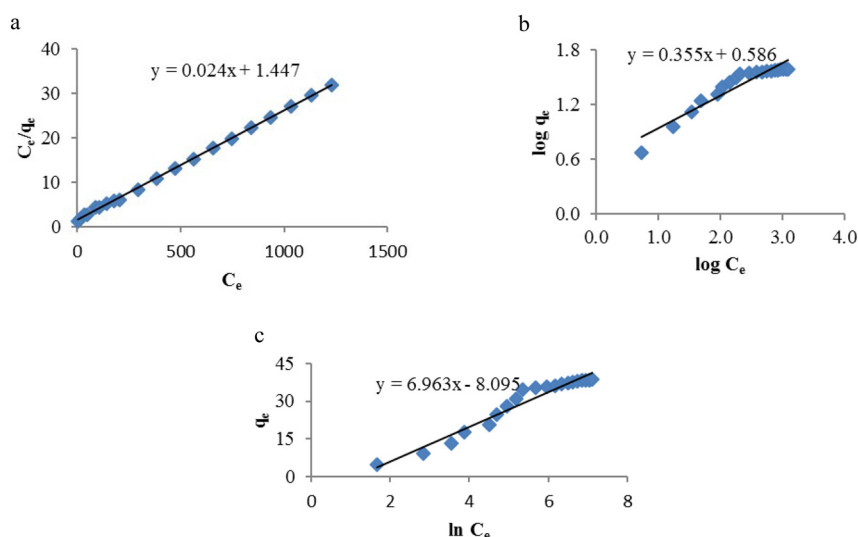


Fig. 5. Adsorption isotherms for Cr (III) adsorption onto WHB a.) Langmuir, b.) Freundlich and c.) Temkin.

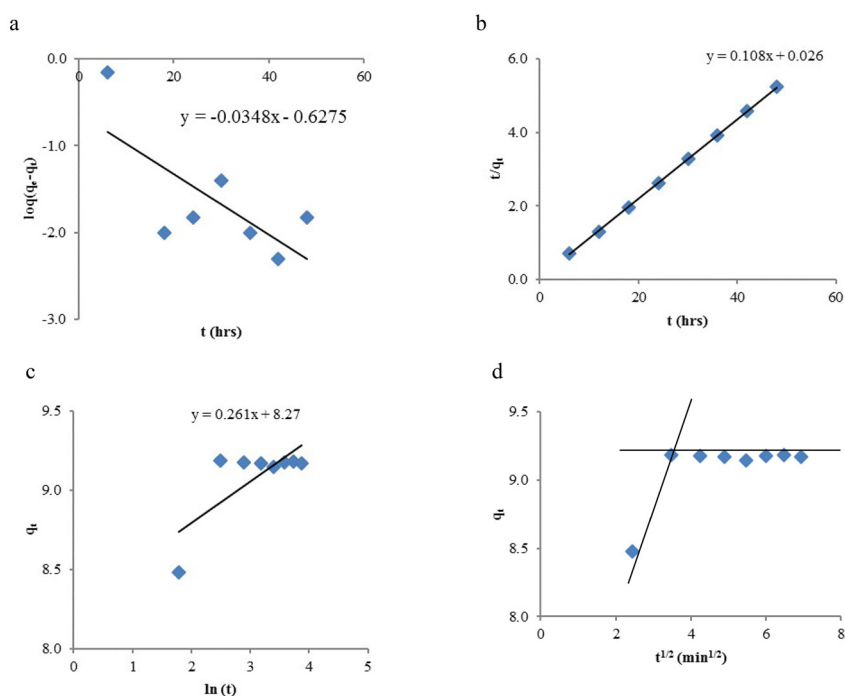


Fig. 6. Adsorption kinetics for Cr (III) adsorption onto WHB a.) First order kinetic model, b.) Second order, c.) Elovich and d.) Intraparticle diffusion.

higher concentration gradient between Cr (III) in the liquid phase (solution) and Cr (III) in the solid phase (adsorbent) as that would increase the number of vacant sites available for adsorption (Gupta *et al.* 2001) and after a considerable time interval, the persisting active sites were hard for utilization by the repellent action between metal ions in solid and liquid phases (Alslaibi *et al.* 2014). Once the surface sorption

sites got exhausted, the rate of Cr (III) adsorption is slower and is determined by rate of its transport from external to internal sites of adsorbent (Anandkumar *et al.* 2009). The kinetic parameters were given in Table 3. The R^2 and q_e value of pseudo second order model suggest that Cr (III) adsorption by WHB could be due to chemisorption (Afshin *et al.* 2019) 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 intraparticle diffusion model. The two linear plots were

Table 2. Isotherm parameters for adsorption of Cr (III) onto WHB.

Constants	
Langmuir isotherm	
q_m (mg g^{-1})	41.7
K_L (L mg^{-1})	0.016
R^2	0.999
Freundlich isotherm	
n (L mg^{-1})	2.82
K_F (mg g^{-1})	3.85
R^2	0.897
Temkin isotherm	
B (J mol^{-1})	6.96
A (L g^{-1})	0.313
R^2	0.949

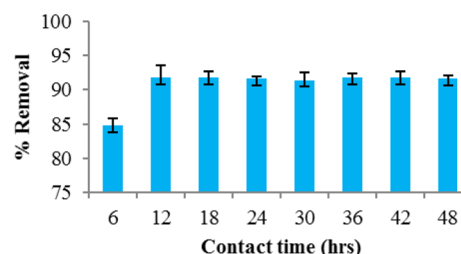


Fig. 7. Effect of contact time on per cent removal of Cr (III).

Table 3. Kinetic parameters for adsorption of Cr (III) onto WHB.

Constants	
Pseudo first order model	
(q _e) _{exp} (mg g ⁻¹)	9.19
(q _e) _{cal} (mg g ⁻¹)	0.24
K ₁ (min ⁻¹)	0.078
R ²	0.501
Pseudo Second order model	
(q _e) _{exp} (mg g ⁻¹)	9.19
(q _e) _{cal} (mg g ⁻¹)	9.26
K ₂ (g mg ⁻¹ min ⁻¹)	0.449
R ²	0.999
Elovich model	
α (mg g ⁻¹ min ⁻¹)	1.505 X 1013
β (g mg ⁻¹)	3.83
R ₂	0.564
Intraparticle diffusion model	
K _{id} (mg g ⁻¹ min ^{-1/2})	0.104
C _i	8.562

obtained from diffusion model which showed that two steps were associated with the sorption of Cr (III) onto WHB. The steps include i) diffusion of Cr (III) ions from solution to WHB surface and ii) further intra particle diffusion (Abdel-Ghani *et al.* 2009).

CONCLUSION

The biochar derived from the aquatic weed exhibited the greater Cr (III) adsorption capacity of 41.7 mg g⁻¹. The adsorption data fitted well in langmuir isotherm (monolayer adsorption of Cr (III) onto WHB) and second order kinetics (chemisorption). This can be utilized for the removal of chromium ions from tannery effluent. Future studies can be carried out to evaluate recovery of adsorbed chromium and recyclability of the adsorbent.

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