

# Adsorption Studies on the Removal of Hexavalent Chromium from Aqueous Solution using Coconut Shell Biochar

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**Abstract** — Adsorption is the most commonly preferred method for heavy metal removal from waste water because of its advantages like low cost, profitability, availability, efficiency and ease of operation. In this study, adsorption potential of coconut shell biochar has been investigated for Cr(VI) removal from aqueous solution using batch and column experiments. Batch adsorption experiments were conducted by varying adsorbent dosage, pH, contact time, temperature and initial concentration. Percentage removal of Cr(VI) using coconut shell biochar is found to be 99.5% at adsorbent dosage of 12g/L, pH 2, temperature of 30°C and at contact time of 1h. Langmuir isotherm model ( $R^2 = 0.9528$ ) were well fitted for coconut shell biochar with maximum adsorption capacity of 2.833mg/g. Adsorption data were well described by pseudo second order model with  $R^2 = 0.9958$ . Intraparticle diffusion model indicated that intraparticle diffusion is not only the rate limiting step. Fixed-bed column study has been carried out to compare results with batch capacities. Expressed through breakthrough curve, fixed-bed Cr(VI) adsorption data shown consistency with ideal S-shape curve. Desorption analysis was performed with 0.2M NaOH. The present study indicated that coconut shell biochar can be used as effective adsorbent for the removal of hexavalent chromium from aqueous solution

**Index Terms**—Batch adsorption, Breakthrough curve, Coconut shell biochar, Cr(VI), Fixed-bed column

## I. INTRODUCTION

Heavy metals emerge from various industrial activities has become significant environmental problems due to their toxic and non-biodegradable nature. Chromium is one of the most abundant and toxic heavy metal that can be seen in earth's crust. Chromium compounds are widely used in the electroplating, metal finishing, leather tanning, metal cleaning, textile dyeing, battery manufacturing, paint, dye manufacturing and chemical manufacturing industries [1]. In natural environment, chromium exists mainly in two oxidation states. They are trivalent chromium, Cr(III) and hexavalent chromium, Cr(VI). Cr(III) is reported as an essential human dietary element whereas Cr(VI) can cause series of health problems from simple skin irritation to lung carcinoma [2]. According to United States Environmental Protection Agency, the maximum permissible limit of Cr(VI) to discharge in

inland surface waters is 0.1mg/L and in potable water is 0.05mg/L [3]. Thus it is important to remove hexavalent chromium from industrial effluent before discharge into water body or onto land.

Several treatment methods have been utilized for Cr(VI) removal including chemical precipitation, ion exchange, electrochemical precipitation, ultrafiltration, biosorption, adsorption, solvent extraction, membrane separation and reverse osmosis[4]. Among these possible techniques, adsorption is one of the most efficient method for Cr(VI) removal due to its simplicity, easiness in handling, sludge free operation, low cost and availability[5].

The search for innovative treatment techniques has focussed attention on the use of biochar from waste biomass for waste water treatment. Biochar is the solid carbon rich material obtained from the thermo-chemical conversion of organic matter in low oxygen environment or in absence of oxygen [5]. It is a value added product which can be used for various application such as crop fertilization, carbon sequestration, soil improvement, environmental remediation of heavy metals and organic pollutants [5,7]. The specific surface area and micropore volume of biochars are much smaller in comparison with activated carbon [6]. However, the adsorption capacity of biochars in regard to hazardous anions and cations are comparable with that of activated carbon. Due to its abundant functional groups and lower cost, biochar is a best replacement of commercial activated carbon [5,8].

Generally, there are different kinds of mechanisms for Cr(VI) removal by adsorbent:

- Electrostatic interaction: Cr(VI) ions are adsorbed on the positively charged surface of sorbent without any Cr(VI) reduction
- Complete reduction: Cr(VI) ions are adsorbed and entirely reduced by sorbent to Cr(III) form
- Cationic adsorption: Cr(VI) ions are entirely reduced by sorbent to Cr(III) form and then adsorbed onto the sorbent
- Adsorption coupled with reduction: Cr(VI) ions are

partly adsorbed onto the sorbent and the remainder are reduced to Cr(III) form [8,9].

Coconut shells are available plenty in tropical countries. The utilization of this waste material to biochar helps in recycling waste as well as keeps the ecosystem clean. The main aim of this study is to analyse the potential of coconut shell biochar for the removal of hexavalent chromium from aqueous solution. For that, batch adsorption study of coconut shell biochar was conducted by varying adsorbent dosage, pH, contact time, temperature and initial metal ion concentration. The mechanism of adsorption of Cr(VI) on coconut shell biochar was investigated by adsorption equilibrium study and adsorption kinetic study. Adsorption equilibrium study was investigated by using Langmuir and Freundlich isotherm models. Adsorption kinetic study were analysed by using pseudo first order, pseudo second order model and intraparticle diffusion rate model. Fixed bed column study has been carried out to compare results with batch capacities. Desorption study were conducted to check the regeneration property.

## II. MATERIALS AND METHODS

### A. Material Collection

Coconut shell was collected from local area in Kollam, Kerala. Rinse it with water to remove impurities and dried in sunlight prior to biochar production.

### B. Preparation of Adsorbents

Biochar from coconut shell was prepared using TLUD gasifier method (Fig.1) for 3h at temperature ranging from 350°C to 450°C. It is then crushed and sieved through 500 micron IS sieve.



Fig. 1. TLUD gasifier method for biochar production

Rinse it with water to remove black colour and dried in sunlight for 2 days. The powdered adsorbents were stored in an air tight plastic container.

### C. Preparation of Cr (VI) Solution

Stock solution of Cr(VI) was prepared by dissolving 1.414g of  $K_2Cr_2O_7$  in 500mL distilled water (1000 mg/l). Working Cr(VI) solutions were prepared by appropriate dilution of the stock solution. pH was adjusted to desired value by using dilute solutions of HCl and NaOH.

### D. Batch Adsorption Experiments

Batch adsorption study were conducted to evaluate the effects of adsorbent dosage, pH, contact time, temperature and initial Cr(VI) concentration. All batch adsorption experiments were conducted in 250 ml Erlenmeyer flask with working volume of 100mL on orbital shaking incubator at 150 rpm agitation speed. After desired contact period, flasks were removed and allowed to stand for two minutes. The solution was then filtered through Whatman filter paper 41 to remove adsorbents. The residual Cr(VI) concentration were analysed through an instrument, UV-visible spectrophotometer at 540nm, after complexation with diphenylcarbazide solution [10]. Removal efficiency and amount of adsorption of Cr(VI) were determined by (1) and (2) respectively:

$$\text{Removal efficiency (\%)} = (C_0 - C_e) * 100 / C_0 \quad (1)$$

$$\text{Amount of adsorption (mg/g)} = (C_0 - C_e) * V / M \quad (2)$$

where,

$C_0$ - Initial concentration of Cr(VI) in solution(mg/L)

$C_e$ - Equilibrium concentration of Cr(VI) in solution(mg/L)

V - Volume of solution(L)

M- Mass of the adsorbent(g)

### E. Adsorption Isotherm Study

Batch experiments were carried out by varying the concentration of Cr(VI) from 4 mg/L to 50 mg/L to study adsorption isotherms that helps to identify adsorption mechanism of Cr(VI) ions onto biochar surfaces. Two isotherm models, Freundlich isotherm model and Langmuir isotherm model were applied to simulate the isothermal adsorption data [9]. Langmuir isotherm model is based on three assumptions: (i) All adsorption sites are identical, (ii) Adsorption is limited to a finite (fixed) number of definite localized sites and (iii) All sites are energetically independent of the adsorbed quantity [10]. The linear form of Langmuir isotherm (3) is represented by :

$$C_e / q_e = C_e / q_m + 1 / q_m K_L \quad (3)$$

where,

$C_e$ - Cr(VI) concentration after equilibrium (mg/L)

$q_e$ - Cr(VI) adsorbed onto adsorbent (mg/g)

$K_L$ - Constant for the Langmuir model (L/mg)

$q_m$ - Maximum adsorption capacity of the isotherm model (mg/g)

The essential characteristics of Langmuir isotherm is classified by the term, separation factor ( $R_L$ ) [10].  $R_L$  is necessary for determining whether adsorption is favourable or unfavourable. It is represented by (4):

$$R_L = 1/(1+K_L \cdot C_0) \quad (4)$$

where,

$R_L$ - Separation factor (dimensionless)

$K_L$  = Langmuir constant

$C_0$ = Initial concentration of the adsorbate

Separation factor indicates adsorption nature to be either unfavourable ( $R_L > 1$ ), favourable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or irreversible ( $R_L = 0$ ).

Freundlich isotherm model is based on the assumption that non-ideal adsorption occurs on a heterogeneous surface and that accompanied by the presence of diverse functional groups and various interactions between sorbate [9] and it is represented by (5):

$$\log q_e = \log K_F + 1/n (\log C_e) \quad (5)$$

where,

$C_e$ = Cr(VI) concentration after equilibrium (mg/L)

$q_e$ = Cr(VI) adsorbed onto adsorbent (mg/g)

$K_F$ = Freundlich constant which indicate sorption capacity (mg/g)

$1/n$ = Constant which indicate sorption intensity

#### F. Adsorption Kinetic Study

The kinetics for adsorption of Cr(VI) on coconut shell biochar was studied for their utilization in the treatment of industrial effluents.

The linear equation (6) used for pseudo first order model was:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where,

$q_e$ = Amount of adsorbate adsorbed at equilibrium (mg/g)

$k_1$  = Pseudo first order rate constant ( $h^{-1}$ )

$q_t$  = Adsorption capacity at time t (mg/g)

The linear equation (7) used for pseudo second order model was:

$$t/q_t = (1/k_2 q_e^2) + (1/q_e)t \quad (7)$$

where,

$q_e$ = Amount of adsorbate adsorbed at equilibrium (mg/g)

$k_2$ = Pseudo second order rate constant ( $gmg^{-1}h^{-1}$ )

$q_t$  = Adsorption capacity at time t (mg/g)

#### G. Intra Particle Diffusion Rate Model

The adsorption process on porous solid adsorbent can be considered under three different stages such as external mass diffusion, intra particle diffusion and adsorption on pore surface. Adsorption on pore surface is very fast and cannot account as rate limiting step[11]. Rate limiting step that appears in the adsorption process may be due to the diffusion of the adsorbate into the adsorbent layer. The intraparticle diffusion model was developed by Weber and Morris [11] was used to predict the actual rate controlling step involved in the adsorption process. The linear equation for intra particle diffusion model was

$$q_t = k_p \times t^{1/2} + C \quad (8)$$

where,

$k_p$ = Intraparticle diffusion rate constant ( $mg h^{-1/2} g^{-1}$ )

$C$  = Thickness of boundary layer (mg/g)

#### H. Fixed-Bed Column Experiments

The fixed-bed column studies were carried out in a column made up borosilicate glass with 2cm internal diameter and a height of 25 cm. A known quantity of the coconut shell biochar was packed in the column to yield the bed mass of 6.9 g and effective depth of 3 cm. Glass beads and glass wool were placed at the bottom and top of the adsorbent to provide equal distribution of flow. Column was operated in down flow mode. At first, deionised water was passed through the column, and then, Cr(VI) solution with known initial concentration (4 mg/l) at pH 2 (optimum pH for removing Cr(VI) using coconut shell biochar) at a fixed flow rate (15 ml/min) was passed through the bed using a peristaltic pump. Passing of chromium solution in the bed was continued until there was no further adsorption. Samples were collected at various time intervals and analysed for residual Cr(VI) concentration.

The breakthrough curves showed the performance of fixed-bed column. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of a sorption column. Break through point is the point in time at which effluent concentration reaches maximum allowable concentration to discharge [12]. The point where the effluent concentration reaches 90% of its influent concentration is considered here as the point of column exhaustion. The breakthrough curve is usually expressed by  $C_t/C_0$  as a function of time or volume of the effluent for a given bed depth [12].

The breakthrough volume,  $V_b$  (mL), can be calculated from the following equation:

$$V_b = Q t_{total} \quad (9)$$

where,

$Q$  is the volumetric flow rate (mL/min)

$t_{total}$  is breakthrough time (min).

The value of the total mass of Cr(VI) adsorbed,  $q_{total}$  (mg), can be calculated from the area under the breakthrough curve

$$q_{total} = \frac{Q}{1000} \int_{t=0}^{t=t_{total}} C_{ad} dt \quad (10)$$

where,

$C_{ad}$  is the concentration of metal removal (mg/L).

Equilibrium metal uptake or maximum capacity of the column,  $q_{eq}$  (mg/g), in the column is calculated as the following:

$$q_{eq} (exp) = \frac{q_{total}}{M} \quad (11)$$

where,

$M$  is the mass of adsorbent in the column (g).

Total amount of Cr(VI) ion sent to column is calculated by:

$$M_{total} = \frac{C_0 Q t_{total}}{1000} \quad (12)$$

where,

$C_0$  is initial concentration (mg/L).

Total Cr(VI) removal percentage is equal to ratio of total mass of Cr(VI) adsorbed,  $q_{total}$  and total amount of Cr(VI) ion sent to column

$$\text{Total Cr(VI) removal percentage(\%)} = \frac{q_{total}}{M_{total}} * 100 \quad (13)$$

### I. Desorption Study

Sorption of Cr(VI) on the adsorbent can occur through physical bonding, chemical bonding, ion-exchange or combination of both. In case of sorption by chemical bonding or ion-exchange or combination of the both, the solute can be desorbed effectively by strong desorbing reagent like acid or alkali solutions. Desorption of Cr(VI) from adsorbent is very important in view of industrial applications. In this study, Cr(VI) desorption was performed using 0.2M NaOH. For desorption study, 0.2M NaOH is pass through the saturated column with a flow rate of 5mL/min.

## III. RESULTS AND DISCUSSION

### A. Effect of Adsorbent Dosage

Adsorbent dosage had a very profound effect on Cr(VI) removal. Adsorption experiments were carried out at varying adsorbent dosage (2-14g/L) for coconut shell biochar, while other parameters pH (2), contact time (1h) and initial concentration (4mg/L) were kept constant. The removal of

Cr(VI) by coconut shell biochar as a function of adsorbent dosage is shown in Fig 2. The optimum dosage for removal of Cr(VI) was found to be 12g/L for coconut shell biochar with 99% removal. It was observed from the results that the percentage removal of Cr(VI) increases with increase in adsorbent dosage up to some extent, thereafter with further increase in adsorbent dosage, no appreciable increase in percentage removal was found. When adsorbent dosage increases, more and more binding sites becomes available for the complexation of Cr(VI) ions and this increased the rate of adsorption. However, very slow increase in removal beyond an optimum dosage may be attributed to attainment of equilibrium between adsorbate and adsorbent at the existing operating conditions [13]. Higher adsorbent dosage causes screening effect of dense outer layer of cells, block the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [14].

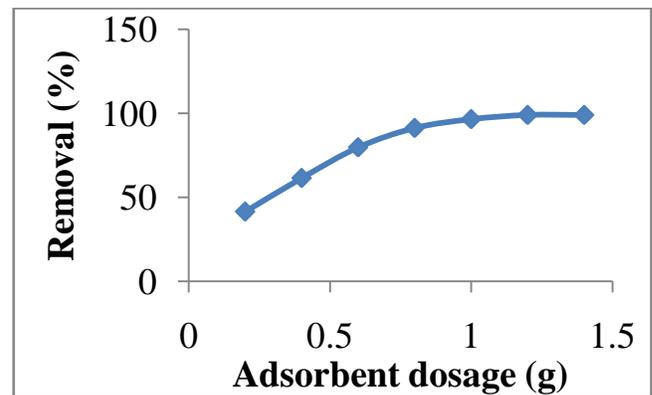


Fig. 2. Effect of Adsorbent dosage

### B. Effect of pH on Cr(VI) Removal

The effect of pH on Cr(VI) removal by coconut shell biochar was investigated at an initial Cr(VI) concentration of 4 mg/l with optimum adsorbent dosage over a pH range of 2–10. The effect of pH is shown in Fig.3. Cr(VI) removal using coconut shell biochar is highly pH dependent. Progressive decrease in Cr(VI) adsorption was observed with increase in pH from 2 to 10. Coconut shell biochar showed maximum removal efficiency of 99% at pH 2. The effect of pH on the adsorption of metal is greatly related to the two main factors: Chemistry of metal in solution, type and ionic state of functional group present in the adsorbent [15]. Chromium solution contains larger number of  $Cr_2O_7^{2-}$  ions and smaller number of  $HCrO_4^-$  ions in the regions of lower pH. A major fraction of negative sites are occupied by  $H^+$  ions via electrostatic interaction in the regions of lower pH and these positively charged sites of the adsorbent are occupied by  $Cr_2O_7^{2-}$  ions [10]. Hence the maximum chromium removal was observed at lower pH i.e. 2. Higher removal of chromium at low pH may also be due to reduction of Cr(VI) to Cr(III) which was then adsorbed by the adsorbent[9,10].

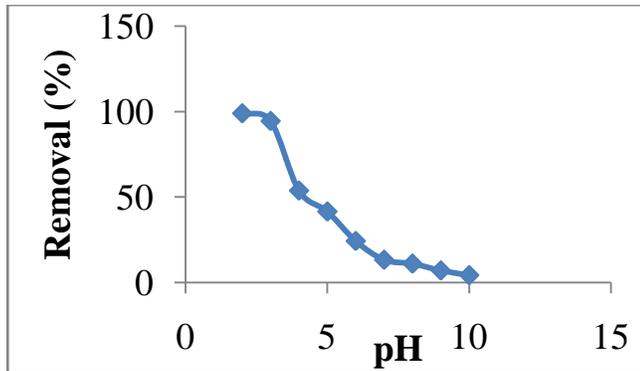


Fig. 3. Effect of pH

### C. Effect of Contact Time

The effect of contact time on Cr(VI) removal by coconut shell biochar was investigated at optimum adsorbent dosage and optimum pH by varying the contact time (15-120min), while other parameters were kept constant. Increase in percentage removal was observed with increase in contact time. Equilibrium time observed was 60min for coconut shell biochar with percentage removal of 99%. There was no appreciable increase in percentage of Cr(VI) removal after these optimum time. As shown in Fig.4, 64% adsorption was completed within first 15min by coconut shell biochar. The rapid initial adsorption may be attributed due to the accumulation of metals on the surface of adsorbent, because of large surface area.

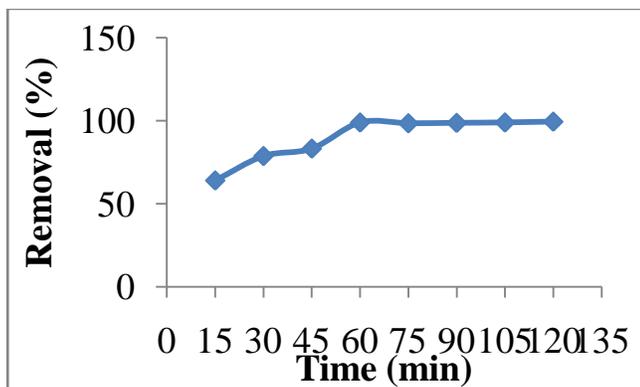


Fig. 4. Effect of Contact time

With the progressive occupation of these sites, process became slower. The adsorption process attained equilibrium in 60min. It may be explained that initially adsorbent showed the fast adsorption which gets slowed down later on, because initially large number of vacant surface sites were available for adsorption and after some time the remaining vacant surface sites were exhausted due to repulsive forces between the solute molecules of solid and bulk phase [16].

### D. Effect of Temperature

Effect of temperature in Cr(VI) removal by coconut shell biochar was performed at different temperature with optimum

adsorbent dosage, optimum pH and optimum contact time, while other parameters were kept constant. The Cr(VI) adsorption capacity of coconut shell biochar was found maximum at temperature of 30°C (Fig.5). Adsorption capacity of coconut shell biochar increases with increase in temperature and decreases after attaining optimum temperature. The increase in the adsorption capacity with the rise of temperature is due to the increase in the number of the adsorption sites generated due to the internal bond breakage near the edge of active surface sites in adsorbents [17].

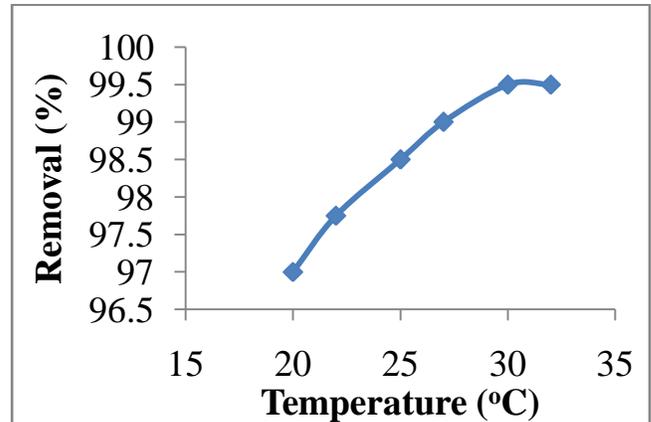


Fig. 5. Effect of Temperature

### E. Effect of Initial Cr(VI) Concentration

Effect of initial concentration on Cr(VI) was carried out at optimized adsorbent dosage, pH, contact time and temperature by varying Cr(VI) concentration from 4-50 mg/L. Adsorption by coconut shell biochar was found to decrease with increase in Cr(VI) concentration from 4-50 mg/L (Fig.6). This is due to increase in number of metal ions competing for available binding sites and due to lack of binding sites for complexation at higher metal ion concentration. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption at 4 mg/L concentration i.e. 99.5% for coconut shell biochar. At higher concentration more chromium ions are left un-adsorbed in the solution due to saturation of adsorption sites [18].

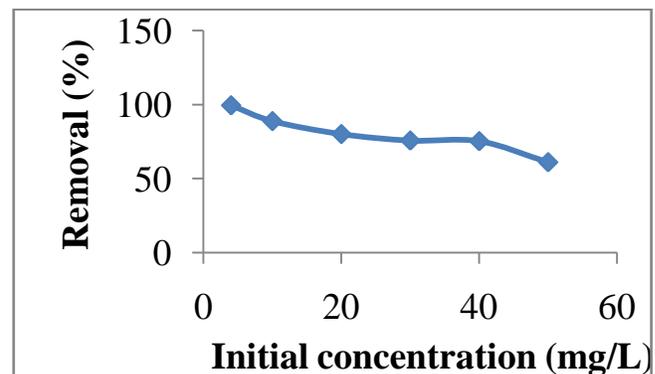


Fig. 6. Effect of Initial concentration

F. Adsorption Isotherm Study

Two adsorption models, Freundlich isotherm model and Langmuir isotherm model were used to study the equilibrium between Cr(VI) ions in solution and Cr(VI) ions adsorbed on the adsorbent surface at constant temperature [11]. The values of the isotherm parameters and the correlation coefficient ( $R^2$ ) of each model are shown in Table I. The value  $R^2=0.9528$  of coconut shell biochar indicated that the adsorption data were well fitted in Langmuir model.

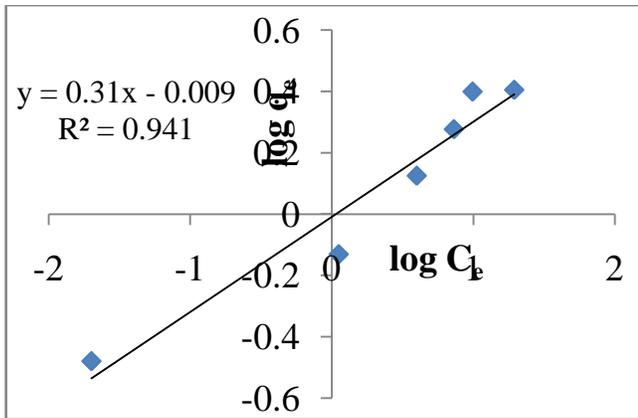


Fig. 7. Freundlich isotherm

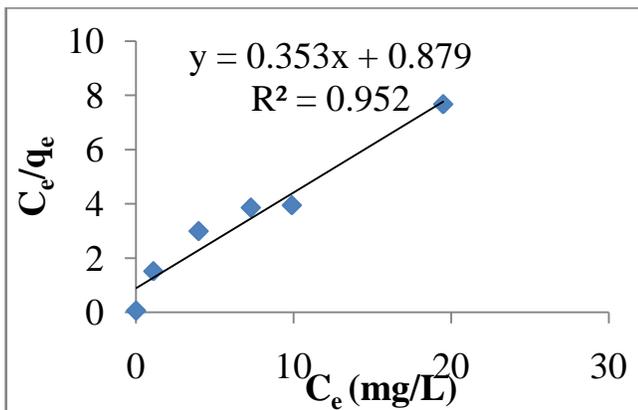


Fig. 8. Langmuir isotherm

TABLE I  
LANGMUIR AND FREUNDLICH ISOTHERM COEFFICIENTS FOR CHROMIUM (VI) ADSORPTION

Adsorbent	Langmuir model			Freundlich model		
	$q_m$ (mg/g)	$K_L$ (L/mg)	$R^2$	$n$	$K_F$ (mg/g)	$R^2$
Coconut Shell Biochar	2.833	0.401	0.9528	3.226	0.979	0.9418

Maximum adsorption capacity of coconut shell biochar was 2.833 mg/g. The high value of correlation coefficient ( $R^2$ ) obtained shows good agreement with experimental values and isotherm parameters, confirming the monolayer adsorption of

Cr(VI) onto the adsorbent. The calculated  $R_L$  values lay between 0 and 1 suggesting that favourable adsorption of Cr(VI) by coconut shell biochar ( $R_L=0.384$ ). The correlation coefficients of Freundlich isotherm model indicated that equilibrium data was not fitted well with it. The values of  $n$  more than 1 indicate favourable Cr(VI) adsorption process [11].

G. Adsorption Kinetic Study

Pseudo first order model and pseudo second order model are used for determining the rate of adsorption and to analyse adsorption process. Straight line graph obtained after plotting  $\ln(q_e - q_t)$  v/s  $t$  and  $t/q_t$  v/s  $t$  shows degree of fitness of metal sorption to pseudo first and pseudo second order rate kinetics model respectively. Adsorption kinetic parameters obtained are presented in Table II. The value of correlation coefficient,  $R^2$  for pseudo first order model was relatively low. And the theoretical  $q_e$  was not agreed well with experimental value (0.33mg/g for coconut shell biochar). Results indicated that Cr(VI) adsorption onto coconut shell biochar was not followed the pseudo first order.

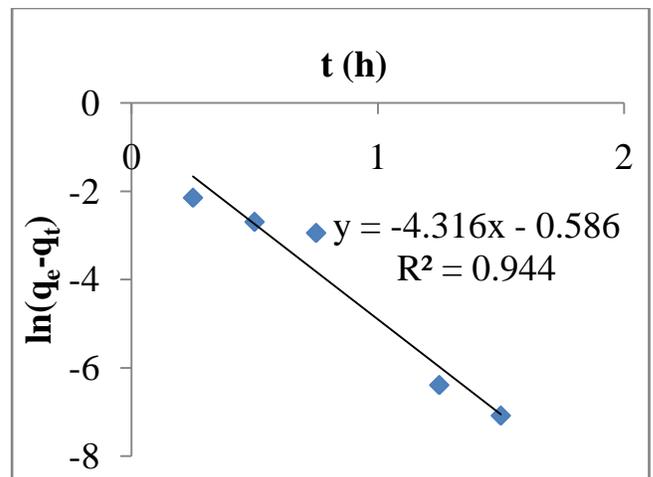


Fig. 9. Pseudo first order

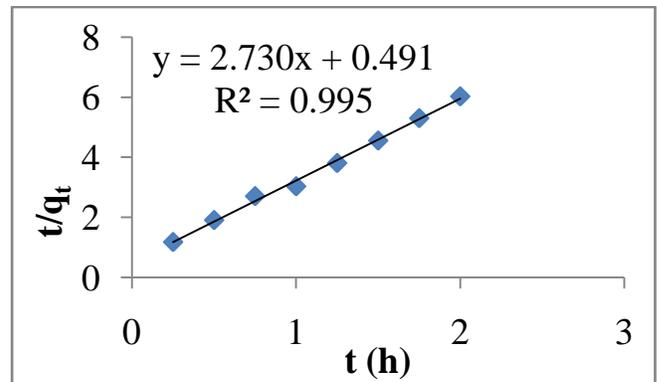


Fig. 10. Pseudo second order

The value of correlation coefficient,  $R^2$  for pseudo second order model was relatively high and the theoretical  $q_e$  was

agreed well with the experimental value. Small difference between the theoretical and experimental values of  $q_e$  may due to the uncertainty inherent in obtaining the experimental  $q_e$  values. This suggests that Cr(VI) adsorption onto coconut shell biochar is highly controlled by the chemisorption behaviour probably related to sharing or exchange of electrons between cation groups of biochars and anion groups of Cr(VI) [10].

TABLE II  
KINETIC PARAMETERS FOR CHROMIUM (VI) ADSORPTION

Adsorbent	Pseudo First Order (PFO)			Pseudo Second Order (PSO)		
	$q_{e,cal}$ (mg/g)	$k_1$ (h <sup>-1</sup> )	$R^2$	$q_{e,cal}$ (mg/g)	$k_2$ (gmg <sup>-1</sup> h <sup>-1</sup> )	$R^2$
Coconut Shell Biochar	0.556	4.316	0.9445	0.366	15.169	0.996

#### H. Intra Particle Diffusion Rate Model

In intraparticle diffusion rate model, linear plot was not passed through the origin indicating that the intra particle diffusion was not only rate controlling step [11]. And some other mechanism also involved in Cr(VI) adsorption along with intra particle diffusion.

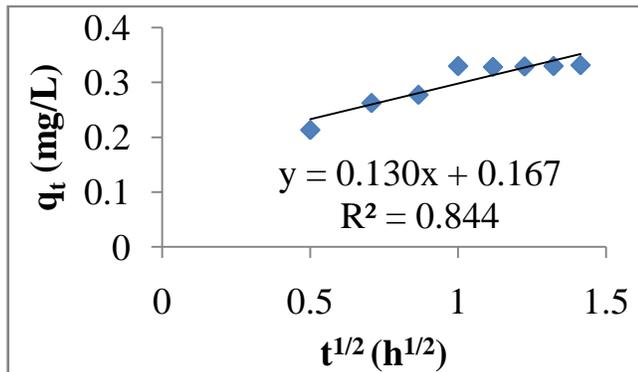


Fig. 11. Intra particle diffusion rate

#### I. Fixed-Bed Column Adsorption Experiments

Break through curve for Cr(VI) removal using coconut shell biochar is shown in Fig.12. It has observed that all Cr(VI) ions were adsorbed initially, resulting zero Cr(VI) concentration in the effluent. The Cr(VI) concentration in effluent gradually rise as adsorption continued. Initially when Cr(VI) containing water is introduced in the down flow mode to clean bed of coconut shell biochar, most of the Cr(VI) removal occur in narrow band at top of the column which is referred to a adsorption zone. As column runs continuously, the adsorption zone move downward through bed as the upper part of column bed become saturated with Cr(VI). Eventually adsorption zone reaches the bottom of column and Cr(VI) concentration starts rising in effluent. In breakthrough curve, the point at which Cr(VI) ion reaches its maximum allowable

value, i.e, 0.05mg/L is referred to as breakthrough point. And the time at which breakthrough point obtained is called breakthrough time. The column was considered to be exhausted when Cr(VI) concentration in effluent reaches 90% of influent concentration. Breakthrough time for coconut shell biochar column was 90min with breakthrough volume of 1350mL. Exhaustion time of column obtained was 660min and volume obtained at this time was 9900mL. Fixed bed adsorption data and parameter for Cr(VI) removal by coconut shell biochar is shown in Table III.

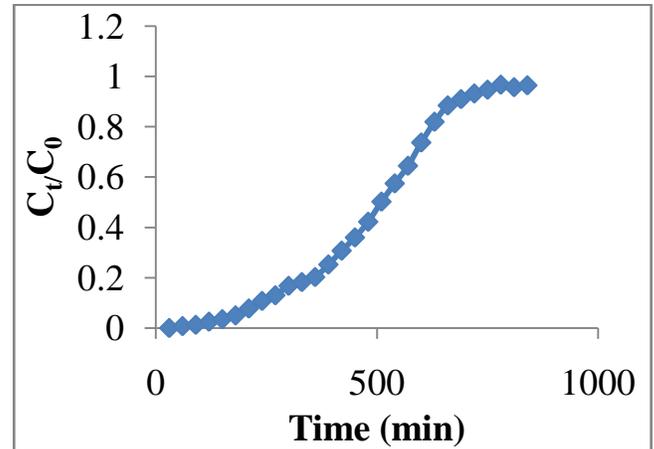


Fig. 12. Breakthrough curve of coconut shell biochar

TABLE III  
FIXED-BED COLUMN ADSORPTION DATA AND PARAMETER FOR Cr(VI) REMOVAL

Adsorbent	$V_b$ (mL)	$V_{exh}$ (mL)	$q_{total}$ (mg)	$q_{eq}$ (exp) (mg/g)	$M_{total}$ (mg)	Cr(VI) Removal (%)
Coconut shell biochar	1350	9900	5.33	0.77	5.4	98.7

#### J. Desorption of Cr(VI) and Regeneration of Adsorbent

Regeneration and recovery of adsorbent material is very important aspects in waste water treatment. It was observed that 300 mL of 0.2M NaOH was required for complete regeneration of coconut shell biochar in 60min.

#### IV. CONCLUSION

The present study demonstrated the potential of coconut shell biochar for Cr(VI) removal from aqueous solution. Batch and column studies were conducted to analyze the potential of coconut shell biochar. Following conclusions were drawn from the results of study:

- Coconut shell biochar show maximum removal efficiency with optimum adsorbent dosage of 12g/L

- Performance of coconut shell biochar is pH dependent and maximum removal efficiency was observed at pH 2
- Adsorption of Cr(VI) reached equilibrium at 60min contact time
- Percentage removal of Cr(VI) using coconut shell biochar is found to be 99.5% at adsorbent dosage of 12 g/L, pH 2, contact time of 1h and at temperature of 30°C
- Adsorption data were well described by Langmuir isotherm ( $R^2=0.9528$ ) than Freundlich isotherm model, confirming the monolayer adsorption of Cr(VI) onto the coconut shell biochar
- Maximum adsorption capacity of coconut shell biochar was found to be 2.833mg/g
- Adsorption kinetics agreed well with pseudo second order model ( $R^2=0.9958$ ) which indicate that coconut shell biochar was highly controlled by the chemisorption
- Intraparticle diffusion rate is not only the rate limiting step
- In fixed bed column study, about 98.7% Cr(VI) removal was achieved with flow rate of 15mL/min and bed height of 3cm
- Spent adsorbent can be chemically regenerated very well by treating it with 0.2M NaOH
- Thus coconut shell biochar is proved to be an effective adsorbent for treating waste water contaminated with hexavalent chromium

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#### REFERENCES

- [1]. R. Jayakumar, M. Rajasimman, C. Karthikeyan, Sorption of hexavalent chromium from aqueous solution using marine green algae *Halimeda gracilis*: optimization, equilibrium, kinetic, thermodynamic and desorption studies, *Journal of Environmental Chemical Engineering* (2014) 1261–1274.
- [2]. Plaska G, Majdan A, Pikus M, Sternik S, Dariusz, Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA, *Chemical Engineering Journal* 179 (2012) 140–150.
- [3]. Zhang X, Zhang L, Li A, Eucalyptus sawdust derived biochar generated by combining the hydrothermal carbonization and low concentration KOH modification for hexavalent chromium removal, *Journal of Environmental Management* 206 (2018) 989–998
- [4]. Chen S , Yue Q , Gao B , Li Q , Xu X , Fu K, Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study, *Bioresource Technology* (2012);113:114–20.
- [5]. Chen T, Zhou Z, Xu, S, Wang H, Lu W, Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge, *Bioresource Technology* (2015) 190, 388–394.
- [6]. Chen T, Zhang Y, Wang H, Lu W, Zhou Z, Zhang Y, Ren L, Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge, *Bioresource Technology* (2014) 164, 47–54.
- [7]. Tan X, Liu Y, Gu Y, Xu Y, Zeng G, Hu X, Liu S, Wang X, Liu S, Li J, Biochar-based nano-composites for the decontamination of wastewater: a review, *Bioresource Technology*(2016) 212, 318–333.
- [8]. Tytlak, A., Oleszczuk, P., Dobrowolski, R, Sorption and desorption of Cr(VI) ions from water by biochars in different environmental conditions., *Environmental Science and Pollution Research*, 22, 5985–5994
- [9]. Zhou L, Liu Y, Shaobo, Yin Y, Zeng G, Tan X, Hud X, Hua X, Jiang L, Ding Y, Liu S, Huang X, Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures, *Bioresource Technology* 218 (2016) 351–359
- [10]. Borna M O, Pirsahab M, Niri M V, Mashizie R K, Kakavandi B, Zare M R, Asadi A, Batch and column studies for the adsorption of chromium(VI) on low-cost *Hibiscus Cannabinus* kenaf, a green adsorbent, *Journal of the Taiwan Institute of Chemical Engineers*(2016) 1–10
- [11]. S. Rangabhashiyam, N. Selvaraju, Efficacy of unmodified and chemically modified *Swietenia mahagoni* shells for the removal of hexavalent chromium from simulated wastewater, *Journal of Molecular Liquids* 209 (2015) 487–497
- [12]. Setshedi K Z, Bhaumik M, Onyango MS, Maity A, High-performance towards Cr(VI) removal using multi-active sites of polypyrrole-graphene oxide nanocomposites:Batch and column studies, *Chemical Engineering Journal* 262 (2015) 921–931
- [13]. Rao M, Parvate AV, AG Bhole, Process Development for removal of copper and lead from aqueous solution by low cost material, *Journal of Environmental Pollution* (2002) 22(1): 17–25.
- [14]. Bishnoi N R, et al. Biosorption of Cu (II) from aqueous solution using algal biomass, *Journal of Scientific & Industrial Research* (2004) 63:813–816.
- [15]. Gupta V K , Shrivastava AK , Jain N, Biosorption of Chromium(VI) from aqueous solutions by green algae *spirogyra* species, *Water Research* (2001);35: 4079–4085.
- [16]. Qaiser S, Saleemi AR, Umar M., Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study, *Journal of hazardous materials* (2009) 166(2-3): 998–1005.
- [17]. H Uzun, Y K Bayhan, Y Kaya, Kinetic and thermodynamic studies of the biosorption of Cr(VI) by *Pinus sylvestris* Linn, *Journal of hazardous materials* 153 (2008) 52–59.
- [18]. Bai S R, Abraham E T., Biosorption of Cr (VI) from aqueous solution by *Rhizopus nigricans*, *Bioresource Technology* (2003) 79: 73–81.