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Environmental Science & Technology**PG and Research Department of Chemistry, Presidency College (Autonomous),  
Chennai-600 005, India**Competitive adsorption of heavy metal ions using Ozone treated rice husk carbon (OTRHC) in Continuous operation****\*S. Sugashini, K. M. Meera Sheriffa Begum**Department of Chemical Engg., National Institute of Technology,  
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**Abstract:** The present investigation deals with the competitive adsorption of metal ions (Ni(II) and Cr(VI)) using ozone treated carbonized rice husk (OTRHC) in continuous process. The effects of process parameters such as flow rate, bed height and influent Cr (VI) concentration were studied to determine the break through time. Adsorption of Ni(II) ions was found to be more when compared to Cr(VI). Theoretical models such as Thomas model, Yoon Nelson model, Adam Bohart model and Bed Depth Service Time model were used to describe the kinetics and interaction behaviour of adsorption in continuous column. The comparison of experimental break through curve with theoretical break through curve was done using error analysis. Regeneration studies were attempted to check the stability and activity of the adsorbent.

**Keywords:** Rice Husk Carbon; Ozone Treatment; Cr (VI); Competitive adsorption; Modelling

**Introduction**

The presence of heavy metals in industrial effluents is accumulating in the ecosystem which causes serious risk to the environment and endangers public health<sup>1</sup>. The use of Chromium and Nickel ions in electroplating industry, steel industry, mining etc., is quite extensive. Cr (III) ions are non-toxic and play an essential role in the metabolism of plant and animals. Cr(VI) ions are highly toxic and intake of Cr(VI) ions leads to carcinogenic problem and other health effects of Cr(VI) ions are the skin allergy, liver problems<sup>2</sup>. Exposure to Ni(II) ions at higher concentration causes lung cancer, nose and bone cancer, head ache, nausea, rapid respiration<sup>3</sup> etc.

Due to its severe toxicity, Environmental Protection Agency Cincinnati OH USA, set the tolerance limit for the discharge of Cr(VI) ions into surface water is 0.1mg/l and in potable water is 0.05 mg/l and for Ni(II) ions the maximum permissible concentration in drinking water should be less than 0.1mg/l<sup>4</sup>. Thus the removal of Cr(VI) ions and Ni(II) ions becomes mandatory.

Various methodologies have been adopted for the removal of heavy metals from industrial waste water such as electro chemical, ion exchange, membrane filtration, reverse osmosis and chemical coagulation, etc., however each method has its own shortcomings and limitations<sup>5,6</sup>.

Adsorption is one of the efficient methods due to its simplicity, sludge free operation; easiness in handling, availability of various adsorbents, adsorbent can be regenerate and more efficient in removal of heavy metals at lower concentration levels<sup>7</sup>.

Activated carbon is a common adsorbent because of its high surface area and easy availability<sup>8</sup>. It is characterized by porous structure and surface chemistry. Surface chemistry influences many properties such as wet ability, catalytic, electrical, electrochemical, adsorption, hydrophilic-hydrophobic etc. Activated carbons were made up of bonding of various heteroatoms, and in particular it constitutes 2-25% of oxygen by weight. Due to this property, the surface of activated carbon can be easily modified to improve the oxygen functional groups by means of oxidation<sup>9,10</sup>.

Recently, ozone a strong oxidizing agents were used to activate the carbon, because of its stability and regenerating ability by chemical treatments. Most of these literatures were with preparation and characterization of ozone treated activated carbon and few literatures with application of ozone treated activated carbon in batch process<sup>11-14</sup>.

In our previous research, rice husk was used as a precursor for the preparation of carbon and followed by activation with ozone treatment. Characterization was done to determine the surface morphology and applied for the removal of hexavalent chromium from aqueous solution in batch adsorption processes.

As concerned with commercialization, it is essential to investigate the sorption studies in continuous phased manner. Fixed bed column for continuous adsorption studies is an efficient process for industrial application<sup>15-17</sup>.

Hence this present study elucidates the feasibility of ozone treated carbonized rice husk as adsorbent for the removal of Ni (II) and Cr (VI) ions in continuous process and also studied the regenerating ability of the adsorbent. The effects of process parameters such as flow rate, bed height and influent Ni (II) and Cr (VI) concentration were studied to determine the break through time. Theoretical models such as Thomas model, Yoon Nelson model, Depth Service Time model were used to describe the kinetics and interaction behaviour of adsorption in continuous column. The comparison of experimental break through curve with theoretical break through curve was done using error analysis.

## Materials and methods

### Materials

Raw rice husk was purchased from the local rice mill. Potassium dichromate was used for the preparation of Cr (VI) stock solution. The pH of the solutions was maintained by hydrochloric acid - potassium chloride for the range of pH 1-3, acetic acid - sodium acetate for the range of pH 4-6 and boric acid - sodium hydroxide for the range of pH 8-10<sup>18</sup>. Analytical grade reagents of 1-5, diphenylcarbazide and acetone were used for analyzing the chromium ions. Double distilled water was used for preparing all the solutions.

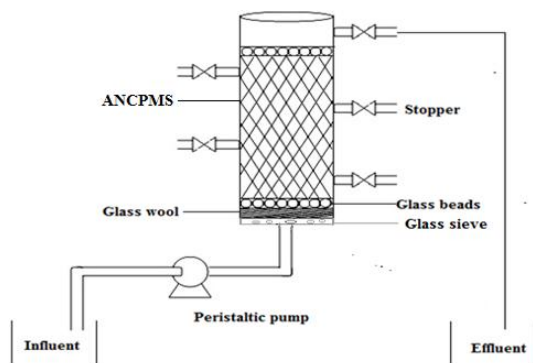
### Preparation of ozone treated rice husk carbon (OTRHC)

Steam activation process was employed for preparing carbon from rice husk in a horizontal tubular furnace. Rice husk was soaked in water for overnight and then filtered to remove the excess water. Wet rice husk was carbonized at 800°C under the reduced atmosphere for 100 minutes. The moisture on the rice husk was employed as the activant. Ozone was generated in an in-house plasma reactor operating at an atmospheric pressure. The reactor was operated at 20 KV and 50 Hz and a typical discharge gap between the electrodes is 3.5 mm. 500 ml of air was passed between the discharge gap and typical applied power was around 3W. The ozone concentration was obtained around 1100 ppm which was measured with an ozone monitor that works based on UV absorption at 254 nm (API-450, NEMA). The carbon samples were placed at the outlet of the reactor and allowed to react with ozone for 12 hrs under room temperature.

### Fixed bed column studies

The continuous adsorption studies were conducted in a glass column with internal diameter of 15 mm and length of 400mm. OTRHC was packed between the glass wool and glass beads in order to prevent the wash out of the adsorbent and is shown in Fig. 1. A known concentration of Cr (VI) solution was fed into the column in up-flow manner at the desired flow rate, bed height and pH. Samples were collected from the exit of the

column at different time intervals. The collected samples were analysed for Cr (VI) ions using a UV Spectrophotometer (JASCO) at a wavelength of maximum absorbance of 540 nm.



**Fig. 1** Schematic representation of continuous adsorption process

### Desorption and regeneration studies

Regeneration studies were conducted to test the reproducibility of the adsorbent. 1M NaOH solution was introduced into the column for desorption of Cr (VI) ions from ozone treated carbonized rice husk. Sample was washed and neutralized with distilled water. The regenerated adsorbent sample was reused in the next cycle of the adsorption experiments. The adsorption - desorption studies were conducted for four cycles.

### Results and Discussion

Ozone treated rice husk carbon (OTRHC) was chosen as adsorbent for the competitive adsorption of Ni(II) and Cr(VI) ions from aqueous solution in continuous process. Continuous column experiments were conducted for various flow rates, bed heights and initial metal ion concentrations at pH 4.0 since the removal of Ni(II) ions and Cr(VI) ions were more efficient in acidic range.

At pH 4, the uptake capacity of Ni(II) ions was observed to be maximum because of ion exchange mechanism between the adsorbent and Ni(II) ions. At higher pH, the entire active sites of the OTRHC were occupied by basic functional groups. Hence the repulsion between the positively charged metal ions and basic functional groups was occurred for Ni(II) ions. The surface positive functional groups of OTRHC adsorbent carried the oxyanions (negatively charged) of Cr(VI) ions by electrostatic force of attraction. Hence for this study, pH 4 was kept constant at all continuous adsorption experiments under various operating conditions for the competitive removal of Ni(II) and Cr(VI) ions from aqueous solution.

The results obtained in the continuous adsorption of Ni(II) and Cr(VI) ions using OTRHC such as break through time, bed exhaustion time, mass transfer zone length, percentage removal and adsorption capacity for various influent concentrations, flow rates and bed heights are presented in Tables 1 and 2 respectively.

**Table 1** Column data analysis at various operating parameters for Ni(II) ions adsorption using OTRHC

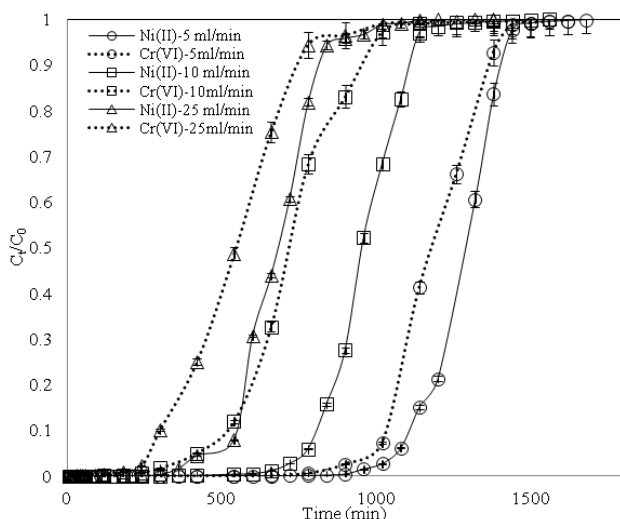
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$t_b$ (min)	$t_e$ (min)	$\Delta t$ (min)	$Z_m$ (mm)	% removal	$q_{total}$ (mg/g)	$q_e$ (mg/g)
100	5	250	960	1500	540	90	84.4	633.6	111.1
200	5	250	840	1440	600	104.1	74.6	1072.0	188.0
300	5	250	660	1320	660	125	69.3	1373.9	241.0
100	10	250	720	1260	540	107.9	76.8	966.4	169.5
100	25	250	420	1020	600	147.8	71.8	1815.5	318.5
100	5	150	840	1380	540	58.5	77.8	536.5	130.7
100	5	100	660	1140	480	42.1	74.8	426.7	152.3

**Table 2 Column data analysis at various operating parameters for Cr(VI) ions adsorption using OTRHC**

$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$t_b$ (min)	$t_e$ (min)	$\Delta t$ (min)	$Z_m$ (mm)	% Removal	$q_{total}$ (mg/g)	$q_{eq(exp)}$ (mg/g)
100	5	250	900	1440	540	56.3	81.7	588.4	143.5
200	5	250	660	1260	600	71.4	70.8	891.6	217.4
300	5	250	420	1020	600	88.2	64.1	978.5	238.6
100	10	250	660	1440	780	81.2	74.2	1069.6	260.9
100	25	250	540	1380	840	91.3	64.3	2219.1	541.2
100	5	150	660	1140	480	42.1	72.9	409.2	146.1
100	5	100	420	900	480	26.6	65.2	293.6	190.7

### Effect of Flow rate

The effect of flow rate on simultaneous adsorption of Ni(II) and Cr(VI) ions were established by varying the flow rates from 5ml/min to 25ml/min at an initial concentration of 100mg/l, bed height of 250mm and pH of 4.0 using OTRHC and their breakthrough curves are shown in Fig. 2.

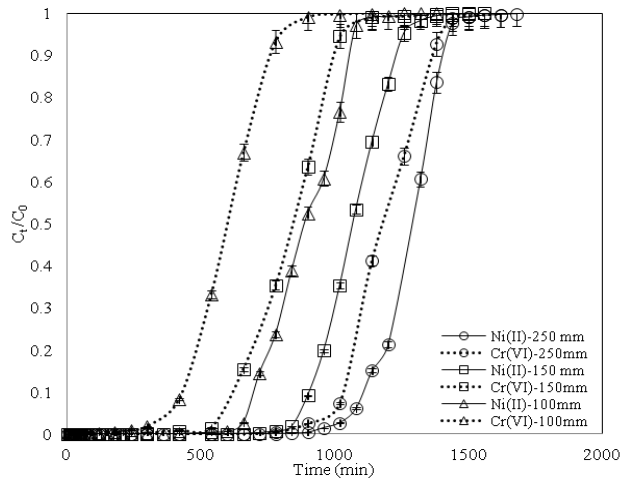


**Fig. 2. Breakthrough curves for the adsorption of Ni(II) and Cr(VI) ions using OTRHC at various flow rates**

It was observed that the column performed well at lower flow rates for both the Ni(II) and Cr(VI) ions. At higher flow rate, the breakthrough and exhaustion time reached faster and this may be due to the insufficient residence time of the metal ions with OTRHC. Also it was found that the diffusion of metal ions was increased at lower flow rate than the high flow rate. The breakthrough time, bed exhaustion time and percentage removal of metal ions using OTRHC were decreased but the mass transfer zone length and the adsorption capacity were increased with increased flow rate. The maximum percentage removal and adsorption capacity were observed for Ni(II) ions when compared to Cr(VI) ions using OTRHC were obtained as 84.4% and 81.7% respectively as given in Tables 1 and 2. Slight variation in percentage removal observed. Hence OTRHC was efficient in adsorbing both cationic and anionic pollutants.

### 3.2 Effect of bed height

The influence of bed height on the adsorption of metal ions using OTRHC were determined by varying the bed heights from 100mm to 250mm at an initial concentration of 100mg/l, flow rate of 5 l/min at pH 4.0 and the results are shown in Fig.3.



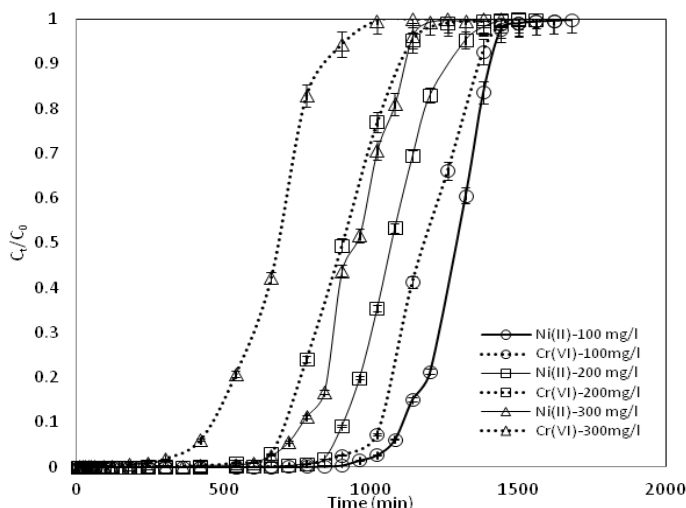
**Fig. 3. Breakthrough curves for the adsorption of Ni(II) and Cr(VI) ions using OTRHC at various bed heights**

It was indicated that the breakthrough time and exhaustion time were increased with increased in bed heights for the adsorption of metal ions. This may be due to the sufficient amount of OTRHC were provided to contact Ni(II) and Cr(VI) ions. The data from Tables 1 and 2 also indicated that the decreased adsorption capacity, increased percentage removal and the broadened mass transfer zone were obtained at increased bed heights. The decrease in adsorption capacity might be attributed to the shortage of metal ion concentration in the solution since the initial metal ion concentration was kept constant for all varying dosage.

The increase in percentage removal might be attributed to the complete utilization of all active sites in the adsorbent dosage by metal ions. The slope of the breakthrough curve decreased with increased bed heights leads to broaden the mass transfer zone.

#### Effect of initial metal ion concentration

The effect of initial metal ion concentration on adsorption of Ni(II) and Cr(VI) ions was performed by varying the initial concentrations from 100mg/l to 300mg/l using OTRHC and the results are shown in Fig. 4.



**Fig. 4. Breakthrough curves for the adsorption of Ni(II) and Cr(VI) ions using OTRHC at various initial concentrations**

It was observed that the breakthrough time and exhaustion time were occurred slowly at lower initial metal ion concentrations and also the treated volume of metal ions also larger at low initial concentrations.

This may be due to the lower concentration gradient which leads to decrease in mass transfer coefficient. The steeper breakthrough curve, lower break through time and lower exhaustion time were obtained at higher inlet concentration of metal ions. This may be due to the change in concentration gradient affects the

saturation rate and breakthrough time. Hence this result demonstrates that the diffusion process is highly dependent on concentration

### Kinetic modelling for adsorption of Ni (II) and Cr (VI) ions by OTRHC

Various theoretical models in continuous adsorption like Thomas model, Yoon Nelson model, Adam Bohart model and Bed depth service time model were fitted with experimental data to determine the solute interaction behaviour in the system.

#### Thomas Model

The data obtained from the experiments were used to calculate the maximum adsorption capacity of OTRHC and the adsorption rate constant using Thomas model. Thomas model is a general model for evaluating the column performance and its expression is given by Eq. (7)

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp(k_{Th} q_e m / Q - k_{Th} C_o t)} \quad (7)$$

where  $k_{Th}$  is the Thomas rate constant (ml/min.mg),  $q_e$  is the adsorption capacity of Cr(VI) ions on OTRHC (mg/g),

The experimental data obtained from continuous adsorption of Ni(II) and Cr(VI) ions using OTRHC were fitted with Thomas model and the constants of Thomas model are presented in Table 3.

**Table 3 Constants of Thomas model for Ni(II) and Cr(VI) ions removal using OTRHC**

Thomas constants for Ni(II) ions						
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$k_{Th}$ (l/min.mg)	$q_e$ (mg/g)	$R^2$	SS
100	5	250	0.162	109.1	0.997	0.0004
200	5	250	0.073	190.6	0.997	0.0005
300	5	250	0.052	237.8	0.998	0.0007
100	10	250	0.140	173.3	0.997	0.0005
100	25	250	0.129	327.4	0.995	0.0005
100	5	150	0.149	130.5	0.997	0.0002
100	5	100	0.138	156.1	0.996	0.0002
Thomas constants for Cr(VI) ions						
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$k_{Th}$ (l/min.mg)	$q_e$ (mg/g)	$R^2$	SS
100	5	250	0.120	142.3	0.997	0.0006
200	5	250	0.059	219.9	0.997	0.0001
300	5	250	0.041	226.1	0.997	0.0026
100	10	250	0.104	207.9	0.996	0.0005
100	25	250	0.098	684.6	0.995	0.0001
100	5	150	0.121	146.4	0.997	0.0004
100	5	100	0.138	195.4	0.994	0.0001

It was found that this model fitted satisfactorily with experimental data obtained from continuous adsorption of Ni(II) and Cr(VI) ions using OTRHC.

When the initial concentration was increased, the  $q_e$  value increased and  $k_{Th}$  value decreased because of larger driving force of concentration gradient generated between the Cr(VI) ions on the adsorbents and Cr(VI) ions in the solution. The higher Cr(VI) ion concentration leads to better column performance. The increased flow rate revealed to reduce the  $k_{Th}$  values and increase the  $q_e$  values. It was also observed that the  $k_{Th}$  values decreased and  $q_e$  values decreased when the bed height was increased from 50mm to 250mm.

The maximum adsorption capacity obtained from this model was found to be satisfied with the experimental data. The higher value of  $k_{Th}$  indicated the faster adsorption process that provides the lower adsorption capacity. Hence, the lower flow rates, higher bed heights and lower initial metal ion concentrations are preferable in obtaining the higher adsorption capacity of OTRHC for metal ion adsorption.

### Yoon Nelson model

The Yoon Nelson model expressed by Eq.(8) is based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate breakthrough on the adsorbent.

$$\frac{C_t}{C_0 - C_t} = \exp(k_{YN}t - \tau k_{YN}) \quad (8)$$

$k_{YN}$  is the Yoon-Nelson rate velocity constant (l/min),  $\tau$  is the time in (min) required for 50% adsorbate breakthrough. The  $k_{YN}$  and  $\tau$  is obtained from the plot of  $C_t / (C_0 - C_t)$  vs. time t. Table 3 shows the constants of Yoon Nelson model obtained at various operating parameters. The constants of Yoon Nelson model were predicted by using Eqs. (8) for the continuous adsorption of Ni(II) and Cr(VI) ions using OTRHC and listed in Tables 4.

**Table 4 Constants of Yoon Nelson model for Ni(II) and Cr(VI) ions removal using OTRHC**

Yoon Nelson constants for Ni(II) ions							
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$k_{YN}$ (l/min)	$\tau$ (min)	$\tau_{exp}$ (min)	$R^2$	SS
100	5	250	0.012	1243.7	1260	0.997	0.0004
200	5	250	0.014	1086.5	1080	0.997	0.0005
300	5	250	0.015	903.6	900	0.998	0.0007
100	10	250	0.014	987.9	960	0.997	0.0005
100	25	250	0.015	746.5	720	0.995	0.0005
100	5	150	0.014	1070.4	1080	0.997	0.0002
100	5	100	0.016	874.5	900	0.996	0.0002
Yoon Nelson for Cr(VI) ions							
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$k_{YN}$ (l/min)	$\tau$ (min)	$\tau_{exp}$ (min)	$R^2$	SS
100	5	250	0.0114	1167.3	1200	0.997	0.0006
200	5	250	0.0118	901.6	900	0.997	0.0001
300	5	250	0.0123	618.0	600	0.997	0.0026
100	10	250	0.0117	1058.1	1080	0.996	0.0005
100	25	250	0.0119	904.1	900	0.995	0.0001
100	5	150	0.0121	820.0	840	0.997	0.0004
100	5	100	0.0139	601.8	600	0.994	0.0001

The regression coefficients obtained from Yoon Nelson model for continuous adsorption of Ni(II) and Cr(VI) ions using OTRHC revealed that this model was best fitted with experimental data obtained from the continuous adsorption of metal ions.

The  $\tau$  value was increased with increased bed heights, decreased with increased flow rates and decreased with increased initial concentrations for both Ni(II) and Cr(VI) ions. This is because of rapid saturation of adsorbents in the column. The  $k_{YN}$  value was decreased with increased bed heights for both the adsorbent. This may be due to the more residential time for metal ions at higher bed height to travel through the column heights which results in reduced adsorption rate. The  $k_{YN}$  value was increased with increased initial concentrations. The increase in concentration increases the competition between the Cr(VI) molecules for the adsorption sites, which ultimately results in increased adsorption rate.

The  $k_{YN}$  value was increased with increased flow rates This may be due to the number of metal ions passing through a particular adsorbent was more at higher flow rates which could increase the rate.

The data in Table 4 also indicated that the  $\tau$  values of model were almost similar to the  $\tau_{exp}$ , where  $\tau_{exp}$  is the experimental time required for 50% breakthrough in adsorption.

### Adam Bohart Model

The Adam Bohart model is used for describing initial part of the breakthrough curve. The Adam Bohart model given by Eq. (9) is based on the assumption that the rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species.

$$\frac{C_t}{C_0} = \exp\left(k_{AB}C_0t - k_{AB}N_0\frac{Z}{F}\right) \quad (9)$$

where  $N_0$  is the saturation concentration (mg/ml).  $k_{AB}$  is the Adam-Bohart constant (ml/mg.min),  $F$  is the linear velocity (flow rate / column section area, cm/min). The constants  $N_0$  and  $k_{AB}$  were calculated from the plot of  $C_t/C_0$  against time  $t$ . The constants of Adam Bohart model obtained at various operating parameters of adsorption of Ni(II) and Cr(VI) ions by OTRHC are presented in Table 5. The  $k_{AB}$  values were decreased and  $N_0$  values were increased with increased initial concentrations, bed heights and flow rates. This may be due to the overall system kinetics is dominated by external mass transfer in the initial part of the adsorption of metal ions using OTRHC. Although the Adam-Bohart model provides a simple and comprehensive approach to evaluate the adsorption column test, its validity is limited to the range of conditions.

**Table 5 Constants for Adam Bohart Model for Ni(II) and Cr(VI) adsorption using OTRHC**

Adam Bohart constants for Ni(II) ions						
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$K_{AB}$ ml/mg.min	$N_0$ (mg/ml)	$R^2$	SS
100	5	250	0.138	2.8	0.969	0.016
200	5	250	0.059	5.0	0.958	0.047
300	5	250	0.041	6.5	0.951	0.037
100	10	250	0.106	4.9	0.931	0.041
100	25	250	0.105	10.3	0.889	0.066
100	5	150	0.123	4.1	0.968	0.020
100	5	100	0.130	5.3	0.937	0.037
Adam Bohart constants for Cr(VI) ions						
$C_0$ (mg/l)	Q (ml/min)	Z (mm)	$K_{AB}$ ml/mg.min	$N_0$ (mg/ml)	$R^2$	SS
100	5	250	0.101	46.6	0.974	0.057
200	5	250	0.042	79.7	0.947	0.022
300	5	250	0.023	97.2	0.912	0.040
100	10	250	0.078	88.8	0.954	0.028
100	25	250	0.067	204.6	0.922	0.035
100	5	150	0.120	63.3	0.900	0.071
100	5	100	0.154	48.1	0.872	0.079

### Bed Depth Service Time model

This is the widely used model and it assumes that the rate of adsorption controlled by the surface reaction between the adsorbate and the unused capacity of the adsorbent. The linearized form of BDST model is given by the Eq. (10)

$$t_s = \frac{N_a Z}{C_0 U_0} - \frac{1}{k_{ads} C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \quad (10)$$



where  $t_s$  is the service time (min),  $N_a$  is the adsorption capacity (mg/g),  $U_0$  is the specific velocity (cm/min),  $k_{ads}$  is the rate constant in BDST model (l/mg.min) and  $C_b$  is the breakthrough time concentration of the Cr (VI) ions (mg/l).

The constants of BDST model for the adsorption of Ni(II) and Cr(VI) ions using OTRHC are listed in Table 6. It was observed that the adsorption capacity of the bed per unit bed volume ( $N_0$ ) was decreased with increased in  $C_t/C_0$ . The decrease in adsorption capacity ( $N_0$ ) might be attributed to the shortage of metal ion concentration in the solution at a particular bed height to contact the adsorbents in the column. The larger values of  $K_a$  implies that even at lower bed heights breakthrough may occur at a later time whereas a smaller  $K_a$  needs a higher bed height to avoid earlier breakthrough time.

**Table 6 Constants for BDST Model for the adsorption of Ni(II) and Cr(VI) ions using OTRHC**

$C_t/C_0$	$K_a (\times 10^4), 1/\text{mg min}$		$N_0 (\times 10^{-3}), \text{mg/l}$		$R^2$	
	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)	Ni(II)	Cr(VI)
0.2	32.4	49.1	5.9	24.2	0.997	0.994
0.4	735.0	737.2	5.8	22.9	0.997	0.997
0.6	-619.9	-496.8	5.5	22.8	0.997	0.997
0.8	-18.0	-13.8	5.4	22.2	0.997	0.997

### Comparison of models with error analysis

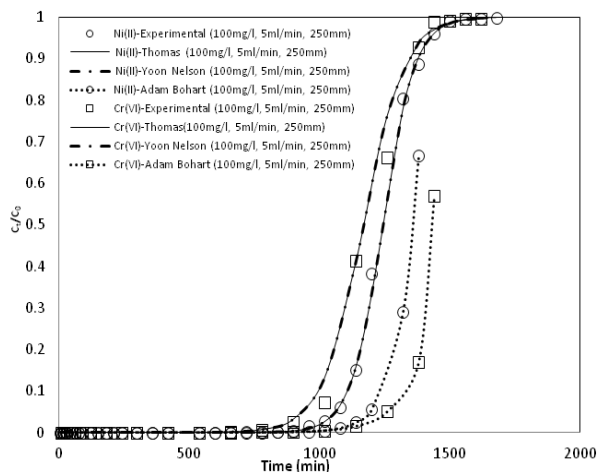
The least square of error analysis<sup>20</sup> was used to compare the models. The mathematical equation was given by Eq. (10)

$$SS = \frac{\sum [(C_t/C_0)_c - (C_t/C_0)_e]^2}{N} \quad (10)$$

where  $(C_t/C_0)_c$  is the ratio of effluent and influent Cr (VI) concentration obtained from the models,  $(C_t/C_0)_e$  is the ratio of effluent and influent Cr (VI) concentration obtained from experiment and N is the number of experimental points. If data from model are similar to the experimental data then SS would be a small number and vice versa. In linear analysis the different forms of equation would affect coefficient of determination ( $R^2$ ) value significantly and it will affect the final determination. This can be avoided by using least square of error analysis. Fig. 5 show the comparison between break through curves between experimental and theoretical models of Ni(II) and Cr(VI) ions for various inlet concentrations at fixed pH of 4.0, bed height of 250mm and flow rate of 5ml/min.

It was observed that the Thomas and Yoon Nelson models were almost merged with the breakthrough curves of experimental data for both the adsorbents. The Adam Bohart model was fitted with initial breakthrough time of the experimental data.

This reveals that the Adam Bohart model is valid for the relative concentration up to 0.5. Larger values were obtained between the Adam Bohart Model and experimental data above the relative concentration of 0.5. Correspondingly the Sum of Squares (SS) analysis also showed that the values of Thomas and Yoon Nelson models were found to be very low and almost identical, however the values of Adam Model was slightly larger compared to Thomas and Yoon Nelson models. Similar trends of theoretical models were observed for all other operating parameters



**Fig. 5. Experimental and Theoretical breakthrough curves of Ni(II) and Cr(VI) ions adsorption by OTRHC**

### Regeneration studies

The regeneration efficiency (RE)<sup>19</sup> is calculated from Eq.(15)

$$\% RE = \frac{q_r}{q_0} \times 100 \quad (15)$$

where  $q_r$  and  $q_0$  are the adsorption capacity of regenerated column and original adsorption capacity of the OTRHC. The results obtained at different parameters for the adsorption of Ni(II) and Cr(VI) ions using OTRHC are presented in Table 7.

From the table, it was found that the percentage removal and adsorption capacity for cycle 1 and cycle 2 were almost similar before and after regeneration for both the adsorbents. After cycle 2, the percentage removal and adsorption capacity of both adsorbents were slightly reduced due to which earlier breakthrough time was observed.

**Table 7 Adsorption parameters of the regeneration cycles for the adsorption Cr(VI) ions using OTRHC**

Ni(II) ions						
Cycles	$C_0$ (mg/l)	Q (ml/min)	Z (mm)	% Removal	$q_{eq(exp)}$	%RE
Exp	100	5	250	84.4	111.1	-
1	100	5	250	84.4	111.1	99.9
2	100	5	250	83.9	109.8	94.6
3	100	5	250	79.6	97.4	92.1
4	100	5	250	73.4	79.6	90.3
Cr(VI) ions						
Cycles	$C_0$ (mg/l)	Q (ml/min)	Z (mm)	% removal	$q_e$	%RE
Exp	100	5	250	81.7	143.5	-
1	100	5	250	81.7	143.5	99.9
2	100	5	250	81.4	143.1	99.7
3	100	5	250	77.2	130.0	90.6
4	100	5	250	71.8	110.3	76.8

### Conclusion

Column adsorption of Ni (II) and Cr (VI) ions using OTRHC was performed and it reveals that the earlier break through time was observed for higher flow rate, higher initial metal ion concentration and lower bed height. The adsorption capacity increased with increased metal ion concentration, bed height and decreased with flow rate. The experimental data fitted well with Thomas model and Yoon Nelson model. The break

through curve of Adam Bohart model fitted with initial part of the breakthrough curve of experimental data. The BDST model described the adsorption capacity of the bed per unit bed volume  $N_0$  increased with increase in  $C_t/C_0$ . The regeneration study reveals that the adsorbent is efficient for four cycles. Also OTRHC is efficient in removal of both Ni(II) and Cr(VI) ions

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