

Application of Activated Carbon Prepared from *Sargassum Wightii* (Greville) for Chromium Removal in a Lab Scale Column Study

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ABSTRACT: The adsorption process is an effective technique for the treatment of heavy metals. Activated carbon, a representative adsorbent, has been widely used to remove diverse pollutants, including cationic heavy metals and anionic metals from the aqueous phase. Recently, there is a great interest to improve the adsorption capacity of low-cost adsorbents for remediation of wastewater. Lab scale column study using activated carbon prepared from *Sargassum wightii* (Greville) was performed to optimize the column sorption parameters such as bed height, time, and various flow rates. Bohart – Adams and Thomas models were employed to evaluate the break through point of the sorption process.

KEY WORDS: Adsorption, activated carbon, *Sargassum wightii* and Column sorption

I. INTRODUCTION

Heavy metals are the major pollutants in marine, ground, industrial and even treated wastewaters. Stringent regulations are increasing the demand for new technologies for metal removal from wastewater to attain today's toxicity driven limits [7]. Activated carbon has undoubtedly been the most popular adsorbent used in wastewater treatment. It overcomes the disadvantages of other conventional adsorbents [2]. Though it is too expensive, natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations, may have potential as inexpensive sorbents. Most of the low cost sorbents have the limitation of low sorptive capacity and for the same degree of treatment disposal problems exist. Therefore, there is a need to explore low cost biosorbents having high contaminant sorption capacity [1].

Biosorption columns operated on cycles consist of loading, regeneration, and rinsing [9]. The prediction of the concentration–time profile or breakthrough curve for the effluent was one of the requirements for a successful design of a column adsorption process. The Adams–Bohart, Wolborska and Yoon and Nelson models were used to predict the behaviour of breakthrough curves [11]. Algal biomass has proved to be the best choice for column study [8] as the carboxylic, sulfonic and hydroxyl groups in the polysaccharides present in the algae can easily uptake the heavy metals [6]. A glass column of 2 cm ID and 35 cm length was used with *Turbinaria ornata* as the biomaterial for copper removal [17]. The flow rate strongly influenced the chromium uptake capacity of *Padina boergesenli* which were recorded at 3, 5, 7 and 10 ml/min. The bed depth service time model was used to analyze the experimental data [16]. Adsorption of lead (II) ions onto activated carbon prepared from the marine green *Ulva fasciata sp.* and commercial activated carbon (CAC) was investigated with the variation in the parameters of pH, contact time, lead (II) ions

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concentration and the adsorbent dose [14]. The aim of the present work was to perform a column study with an activated carbon from *Sargassum wightii* to remove chromium from tannery effluent.

II. MATERIALS AND METHODS

Preparation of ZnCl₂ activated carbon using *Sargassum wightii* (Greville)

The dried seaweed *Sargassum wightii* was used to prepare the activated carbon by using varying concentration (10, 20, 30, 40, 50 % (w/v)) of ZnCl₂ [5].

Column study- Column designing and Break through point

A glass column of 15 cm height and 2 cm internal diameter was used to carry out the column studies. Activated carbon prepared from *Sargassum wightii* was employed for the column studies. The column was packed with this activated carbon and the adsorbate solution was pumped up to flow through the bed using a peristaltic pump (Watson Marlow 5200). Experiments were carried out at varying flow rate (5, 10 and 15 ml/minutes) and packed bed height (2, 4, 8 cm) employing chromium solution of initial concentration 100 mg/L. The total quantity of chromium adsorbed in the column (P) was calculated from the area below the breakthrough curve (outlet chromium concentration versus time) multiplied by the flow rate. By dividing P by the biosorbent mass (M) the uptake capacity (q) of the biomass was obtained [3]. The breakthrough time (t_b , min), the time at which chromium concentration in the effluent reached >1 mg/L and bed exhaustion time (t_e , min, the time at which chromium concentration in the effluent exceeded 99 mg/L) were used to evaluate the overall sorption zone (Δt) [18]: $\Delta t = t_e - t_b$. The length of the mass transfer zone (Z_m), also called as critical bed length was calculated from the breakthrough curve (Volesky *et al.*, 2003): $Z_m = Z (1 - (t_b / t_e))$, where, Z is the bed height (cm). Effluent volume (V) was calculated as follows (Aksu and Gonen 2004): $V_{\text{eff}} = F_r t_e$, Where, F_r is the volumetric flow rate (ml/min).

Total amount of chromium pumped to the column (P_{total}) was calculated using the following formula (Aksu and Gonen, 2004): $Cr_{\text{total}} = C_0 F_r t_e / 1000$. The percentage removal of chromium with respect to the flow volume was calculated as follows (Aksu and Gonen 2004): Chromium removal (%) = $Cr_{\text{ad}} / Cr_{\text{total}} \times 100$. Various mathematical models can be used to describe the fixed bed adsorption. Among these, Thomas model is simple and widely used by several investigators [3] and [19]. The linearized form of Thomas model is expressed as follows: $\ln((C_0/C) - 1) = k_{\text{Th}} Q_0 M / F_r - k_{\text{Th}} C_0 t$. where k_{Th} is the Thomas model constant (l/mg h), Q_0 the maximum solid phase concentration of solute (mg/g), V the throughput volume (L). The model constants k_{Th} and Q_0 were determined from a plot of $\ln[(C_e/C_0) - 1]$ against t at a given flow rate [3].

Bed depth service time (BDST) is a simple model, which states that bed height (Z) and service time (t) of a column bears a linear relationship. The equation is expressed as follows [13]: $T = (N_0 Z / C_0 v) - (1/k_a C_0) \ln((C_0/C_b) - 1)$, where, C_b is the breakthrough sorbate concentration (mg/L), N_0 - the adsorption capacity of bed (mg/L), v - the linear velocity (cm/h), and k_a - the rate constant (L/mg/h). The column service time was selected as time, when the effluent chromium concentration reached > 1 mg/L.

III. EXPERIMENTAL RESULTS

Effect of Zinc chloride on the activated carbon yield from *Sargassum wightii*

The increasing concentration of ZnCl₂ from 10 % to 30 % increased the yield (%) of activated carbon from 24.24 % to 35.76 %. When the concentration of the ZnCl₂ was increased beyond that, it led to a decrease in the percentage yield of activated carbon from 35.76 % to 22.54 %. The yield of activated carbon was lesser (12.15 %) without ZnCl₂ treatment (Table: 1).

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Table: 1 Effect of ZnCl₂ concentration on the activated carbon yield (%)

Concentration of ZnCl ₂ (%)	0	10	20	30	40	50
Yield (%)	12.15	24.24	27.16	35.76	25.15	22.54

Column study using activated carbon of *Sargassum wightii*

Effect of flow rate

The effect of flow rate on chromium sorption by activated carbon of *Sargassum wightii* was studied by varying the flow rate from 5 to 15 ml/minutes, while the bed height and initial chromium concentration were held constant at 8 cm and 100 mg/L, respectively. The effects of effluent chromium concentration versus time at different flow rates were plotted (Fig: 1). All the calculated parameters are provided in Table 2. An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 15 ml/minutes. The flow rate also strongly influenced the chromium uptake capacity of activated carbon as 69.788, 73.676 and 84.871 mg/g, which were recorded at 5, 10 and 15 ml/minutes, respectively.

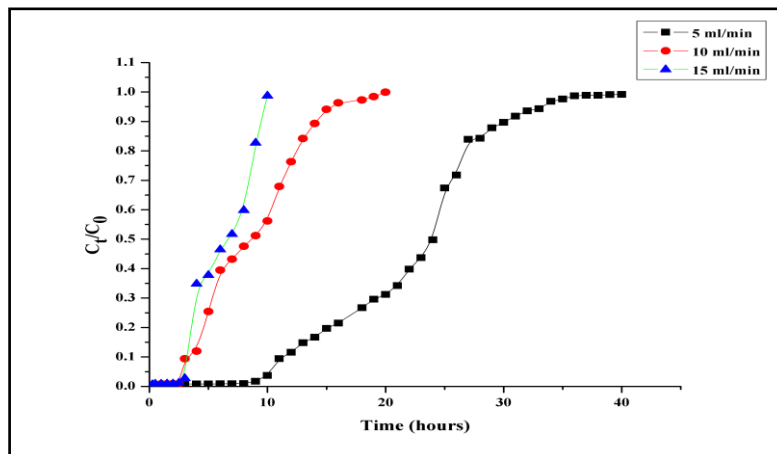


Fig: 1 Effect of flow rates on the break through profile of adsorption of chromium by activated carbon of *Sargassum wightii*

The column data were fitted to the Thomas model to determine the model constant (k_{Th}) and maximum solid phase concentration of solute (Q_0) at different flow rates. The model gave a good fit of the experimental data at all flow rates examined with high correlation coefficients (0.984, 0.987 and 0.992). The values of k_{Th} obtained from Thomas model were 0.0053, 0.0059 and 0.0061 L/mg h at 5, 10 and 15 mL/minutes, respectively. The values of Q_0 obtained from the Thomas model were 49.26, 95.71 and 107.82 mg/g at 5, 10 and 15 ml/minutes, respectively. Thomas constant k_{Th} increased with an increase in the flow rate (Table. 3).

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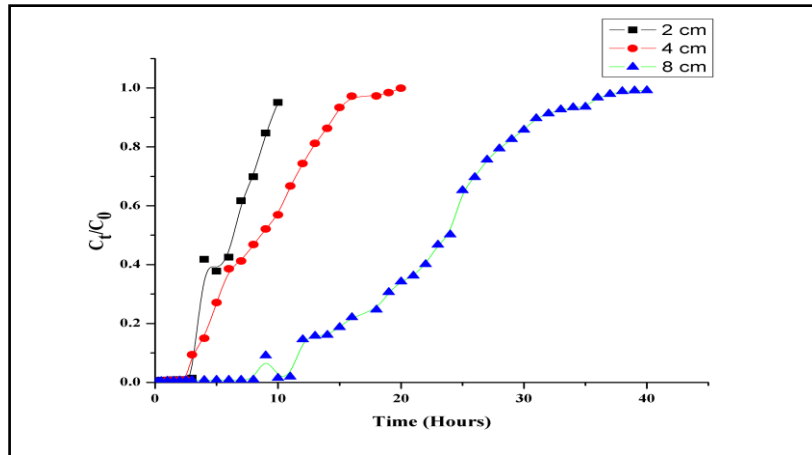


Fig: 2 Effect of bed heights on the break through profile of adsorption of chromium activated carbon of *Sargassum wightii*

Bed height (cm)	Flow rate (ml/min)	Uptake (mg/g)	t_b (h)	t_e (h)	Δt (h)	V_{eff} (L)	Z_m (cm)	Total Cr removal (%)
2	5	69.788	3	10	7	18.9	1.4	74.56
4	5	64.573	4	19	15	62.5	3.16	80.59
8	5	58.762	9	36	27	104.5	5.68	88.84
8	10	73.676	4	20	16	25.12	6.4	79.32
8	15	84.871	2	10	8	44.32	6.96	70.27

Table:2 Biosorption parameters obtained with different bed heights and flow rates

Effect of bed height

Accumulation of chromium in the packed bed column is largely dependent on the quantity of sorbent inside the column. The sorption breakthrough curves were plotted by varying the bed heights from 2 to 8 cm at 5 ml/minutes flow rate and 100 mg/L initial chromium concentration for activated carbon of *Sargassum wightii* (Fig: 2). Both breakthrough and exhaustion time increased with an increase in bed height and resulted in a broadened mass transfer zone, as more binding sites are available for sorption. The percentage removal of chromium was considerably affected by bed height from 74.56 % to 88.84% when the bed height was increased from 2 to 8 cm. This trend was due to the fact that the uptake capacity depends on the amount of sorbent available for sorption. Also, a considerable increasing

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trend was observed for total chromium removal percentages as 74.56, 80.59 and 88.84% for 2, 4 and 8 cm, respectively (Table. 2).

The BDST model is based on physically measuring the capacity of the bed at different breakthrough values. The plot of service time against bed height at a flow rate of 5 ml/minutes was linear ($R^2 = 0.987$) indicating validity of BDST model for the column study of activated carbon of *Sargassum wightii*. The computed N_0 and k_a were 34.63 mg/ml and 0.0064 L/mg/h, respectively. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental run (Table: 3).

Table: 3 Constants of Thomas and Bohart Adams models

S.No	Thomas model				Bohart Adams model		
	Flow rate (ml/min)	k_{Th} (L/mg/h)	Q_0 (mg/g)	R^2	N_0 (mg/ml)	K_a (L/mg/h)	R^2
1.	5	0.0053	49.26	0.984	34.63	0.0064	0.987
2.	10	0.0059	95.71	0.987	-	-	-
3.	15	0.0061	107.82	0.992	-	-	-

IV. DISCUSSION

The percentage yield of activated carbon increased with an increase in $ZnCl_2$ concentration and at a specific concentration, maximum yield was obtained. After that particular concentration, a decrease in carbon yield was observed (Table. 1). Similar results were observed [10] in studies on the preparation of activated carbons from lignocellulosic materials and oil-palm shells respectively by chemical activation. The effect of concentration of activating agent on the surface area is due to the impregnation ratio. The carbon yield decreases with an increase in the activation temperature, activation time and chemical impregnation ratio using rice husk as raw material [15].

Flow rate is one of the important characteristics in evaluating sorbents for continuous-treatment of phenol containing effluents on an industrial scale (Aksu and Gonen 2004). An increase in flow rate increased the Thomas constant K_{TH} for chromium adsorption using activated carbon of *Sargassum wightii*. Similarly, other researchers were also [4] observed that the increasing flow rate increased the Thomas constant. The metal ion could be stripped by addition of HCl or H_2SO_4 at low pH, making the adsorbent regeneration and its reutilization possible [12]. The breakthrough curve analysis from continuous adsorption studies revealed that the slower breakthrough time reached for lesser initial concentration, slower flow rate, and higher bed height. Bed Height service model and Thomas model were well fitted with the experimental data [13].

V. CONCLUSION

The optimum concentration of $ZnCl_2$ was determined as 30% for the preparation of activated carbon from *Sargassum wightii*. Thomas model for different flow rate and BDST model for different column bed heights have been employed. The model constants determined were proposed for the use in column design. In conclusion, seaweeds can be considered as a potential and low cost natural material for the production of activated carbon due to the easy availability and its suitability for heavy metal adsorption.

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