

# Investigation of Cr(VI) Adsorption by Dried Brown Algae *Sargassum* sp. and Its Activated Carbon

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**ABSTRACT:** *In this research, the batch removal of toxic hexavalent chromium ions from wastewater and aqueous solution using dried (BD) *Sargassum* sp. (brown marine algae) and Activated Carbon (AC) prepared from it was examined. Biomass, pH and the initial concentration of Cr(VI), adsorption models and kinetic studies were investigated. The experiment was performed in a batch system and the effect of solution pH, initial concentration and contact time on biosorption by both biomasses were investigated and compared. When we used AC and BD as biosorbents, optima conditions were established at pH=2.0, Cr<sup>6+</sup> concentration at 3.69 mg/g BD and 6.877 mg/g AC and equilibrium time of 120 min. The adsorption was in the range of 83.55% and 91.98%, respectively. The experimental adsorption data were fitted to the Langmuir adsorption model. The chromium (VI) uptake by the biosorbents was best described by a pseudo second-order rate model.*

**KEY WORDS:** *Sargassum* sp., Activated carbon, Adsorption, Algae, Biosorbent.

## INTRODUCTION

The presence of the toxic heavy metals in water resulting from rapid industrialization and technological advances is a worldwide environmental problem. Removal of these pollutants from aqueous effluents has conventionally been accomplished through abiotic processes [1]. Chromium has both beneficial and detrimental properties. Two stable oxidation states of chromium persist in the environment, Cr(III) and Cr(VI), which have contrasting toxicities, mobilities and bioavailabilities. Cr(III) is necessary for glucose metabolism in human nutrition, whereas most of the hexavalent compounds are toxic.

While Cr(III) is relatively innocuous and immobile, Cr(VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin [2]. Chromium and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textiles, steel fabrication, and canning. These industries produce large quantities of toxic wastewater effluents [3].

The maximum concentration limit for Cr(VI) for discharging into inland surface waters is 0.002 mmol/L, and

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its maximum allowable concentration in potable water is 0.001 mmol/L. A wide range of physical and chemical processes are available for the removal of Cr(VI) from wastewater, such as electrochemical precipitation, ultrafiltration, ion exchange, membranes, evaporation, and reverse osmosis [4-6]. A major drawback with precipitation is sludge production. Ion exchange is considered a better alternative technique. However, it is not economically appealing because of high operational costs [34]. Adsorption using Commercially Activated Carbon (CAC) can remove heavy metals such as cadmium [7], chromium [8], copper [9], and nickel [10] from wastewater. However, CAC remains an expensive material, and the higher the quality of the activated carbon, the greater its cost [11]. AC has many applications, one of which is as an adsorbent for the purification of water, air and many other chemical products. AC has been an effective adsorbent for dye removal. Adsorption capacity of certain carbon is known to be a function of porous structure, chemical nature of the surface and pH of the aqueous solutions. Surface functional groups play an important role in deciding the adsorption capacity and removal of the adsorbents [36]. Kindasa Water Services (KWS) currently operates an RO facility at Jeddah Port on the Red Sea in Saudi Arabia, using conventional pre-treatment, to provide a 14 mld output. Due to an increasing requirement for treated water services, a contract has recently been placed with Weir Westgarth for a new desalination facility to expand the capacity of RO treated water from 14 to 40.5 mld (3.7 to 10.7 MGD). The original system has operated well for most of the time since it was brought into supply in 2000. However, occasional poor quality conditions have occurred during storms, or periods of algal bloom, which have resulted in SDI's to the RO exceeding target levels. Accordingly, an interest was expressed in utilizing UltraFiltration (UF) as an alternative to conventional pre-treatment, to improve RO feed quality, and guarantee on-stream time. The UF trial was highly successful in achieving stable membrane permeability and a consistent filtrate SDI when operated under optimized process conditions. Utilizing ferric chloride dosing, with acidification, the trial has operated at a flux of 95 l/mh, and at a transmembrane pressure of 0.15-0.20 bar. The recovery was 94% [37].

Therefore, searching for low-cost activated carbon

and other adsorbent materials is of great important to wastewater treatment [12]. In recent years, development of surface-modified activated carbon has generated a diversity of activated carbon with far superior adsorption capacity. Coconut husk and palm pressed fibers can be used in this way to remove metal and reduce the cost of waste disposal [13]. Filtration is the passive uptake of heavy metals from aqueous solutions by biological materials. Filtration uses the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or purely physicochemical pathways of uptake [22]. The mechanisms by which microorganisms remove metals from solutions are (1) extracellular accumulation/precipitation, (2) cell-surface sorption or complexation, and (3) intracellular accumulation [14]. The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth, and the environmental conditions during the filtration process (such as pH, temperature, and presence of certain co-ions) are important parameters that affect the performance of a living biosorbent. The efficiency of the biosorbent is also influenced by the chemical features of the metal solution [15]. Potent biosorbents are easily available in algae, fungi, and bacteria. A source of low-cost biomass produced in great quantities is marine macroalgae. Recent studies about the filtration of toxic metals by algae are focused on toxicological aspects, metal accumulation, and pollution indicators in relation to filtration by living (metabolically active) biomasses [35]. The objective of the present work is to evaluate the potential of dried and activated carbon forms of *Sargassum* sp. for chromium uptake.

## EXPERIMENTAL SECTION

### *Dried Biomass*

*Sargassum* sp., was collected from the Persian Gulf on the coast of Queshm, Iran. The biomass of alga was transferred to the laboratory, washed with deionized water to wash out any mineral contaminants, and dried [38,39].

### *AC and MD preparation*

AC Preparation: 120 g of brown algae *Sargassum* sp. was added in small portions to 96 mL of 97% HCl. The resulting mixture was kept for 24 h at room temperature followed by refluxing in fume hood for 4 h. After cooling, the reaction mixture was washed

**Table 1: Langmuir and Freundlich constants for biosorption of Cr(VI) using BD and AC from Sargassum sp.**

Two-parameter models		BD			AC		
		0.4g	0.6g	0.8g	0.4g	0.6g	0.8g
Langmuir	Q <sub>m</sub> (mmol/g)	0.006	0.080	0.020	0.150	0.060	0.060
	b (mmol/L)	0.003	0.0002	0.0009	0.001	0.005	0.008
	R <sup>2</sup>	0.021	0.021	0.021	0.021	0.020	0.020
Freundlich	K <sub>ef</sub> (L/mol)	0.010	0.00006	0.0855	0.002	0.010	0.015
	n	2.092	0.989	1.356	1.290	1.545	1.957
	R <sup>2</sup>	0.996	0.946	0.997	0.998	0.999	0.881

repeatedly with deionized water and soaked in 2% NaHCO<sub>3</sub> solution to remove any remaining acid, and pH of the activated carbon reached to 7. The solution was then dried in an oven at 150° C for 48 h. The powdered materials were then used as adsorbents for study. The powdered materials were then sieved. Materials with particle sizes in the range of 0.3 mm to 1 mm were used in the present study and kept in a glass bottle until used. MD Preparation: The samples were then grounded to an average particle size of 0.5-1 mm.

#### Preparation of synthetic solution

The stock solution of Cr(VI) (1000 mg / L) was prepared in deionized water with potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>). All working concentrations were obtained by diluting the stock solution with deionized water, and pH was adjusted to the desired values according to the following experimental design with 1 M HCl and 1 M NaOH solutions.

#### Adsorption experiments

A series of flasks containing dichromate solutions varying in concentration from 0.2 to 1.3 mmol/L were prepared from the stock solution. Adjustment of pH was carried out using 1 N NaOH and 1 N HCl. Batch equilibrium sorption experiments were carried out in 250 mL erlenmeyer for 120 min (0.2–0.8 g of biomass, 30 mL of metal solution) in a rotary shaker. These experiments were done at pH 2.0–9.0. After the sorption equilibrium was reached (120 min), the solution was separated from the biomass by membrane filtration. The initial and equilibrium chromium concentrations in each flask were determined by Atomic Absorption Spectrometry (AAS). To maximize Cr removal by the adsorbent, batch experiments were conducted at a constant temperature

using the optimum conditions of all pertinent factors, such as dose, pH, initial concentration, and contact time. Subsequent adsorption experiments were carried out using only the optimized parameters.

#### Equilibrium isotherm

##### Chromium Uptake Capacities and Sorption Isotherm

The amount of metal adsorbed by activated carbon was calculated from the difference between the metal quantity added to the biomass and the metal content of the supernatant using the equation

$$q_e = (C_0 - C_e) V / M \quad (1)$$

Where  $q_e$  is the metal uptake (mg metal adsorbed per g adsorbent),  $C_0$  and  $C_e$  are the initial and equilibrium metal concentrations in solution (mmol/L),  $V$  is the volume of the solution (mL), and  $M$  is the weight of activated carbon (g). To examine the sorbed and aqueous concentration at equilibrium, sorption isotherm models and Langmuir and Freundlich adsorption models were used for the data. These isotherm constants for Cr(VI) are presented in Table 1.

##### Freundlich adsorption model

The Freundlich model [16] habitually gives a better fit for adsorption from liquids and can be expressed as

$$q_e = K_f C_e^{1/n} \quad (2)$$

In this model, the rate of adsorption is dependent on of the constants  $1/n$  and  $K_f$  (L / g). For a good adsorbent,  $0.2 < 1/n < 0.8$ , and a smaller value of  $1/n$  shows better adsorption and formation of a rather strong bond between the adsorbate and the adsorbent. Many researchers have used this model to interpret this sorption data for various systems [17-20].

### Langmuir adsorption model

The most widely used isotherm equation for modeling equilibrium is the Langmuir equation. It is assumed that there is a finite number of binding sites that are homogeneously shared over the adsorbent surface. These binding sites have the same adsorption of a single molecular layer, and there is no interaction between adsorbed molecules. The saturated monolayer isotherm can be represented as

$$q_e = bq_{\max} C_e / (1 + bC_e) \quad (3)$$

Where  $q_e$  is metal ions adsorbed (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $q_{\max}$  is the maximum adsorption capacity, and  $b$  is an affinity constant;  $q_{\max}$  represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance, in cases where the sorbent did not reach its full saturation in experiments and  $b$  is constantly related to the affinity of the binding sites [21, 22, 40].

### Adsorption kinetic studies

The kinetics of adsorption describes the rate of chromium ion uptake on activated carbon prepared from *Sargassum*, which controls the equilibrium time. These kinetic models included the first-order and second-order equations.

#### Pseudo first-order model

The pseudo first-order rate expression is described by the equation

$$dq_t/dt = k_1 (q_e - q_t) \quad (4)$$

Where  $q_e$  is chromium sorbed at equilibrium per unit weight of sorbent (mg/g),  $q_t$  is chromium sorbed (mg/g), and  $k_1$  is the rate constant ( $\text{min}^{-1}$ ) [22]. The integrated form of Eq. (4) becomes

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t \quad (5)$$

A plot of  $\log(q_e - q_t)$  versus  $t$  indicates a straight line of slope  $(k_1/2.303)$  and an intercept of  $\log(q_e)$ .

#### Pseudo second-order model

The sorption data also analyzed a pseudo second order [22], given by

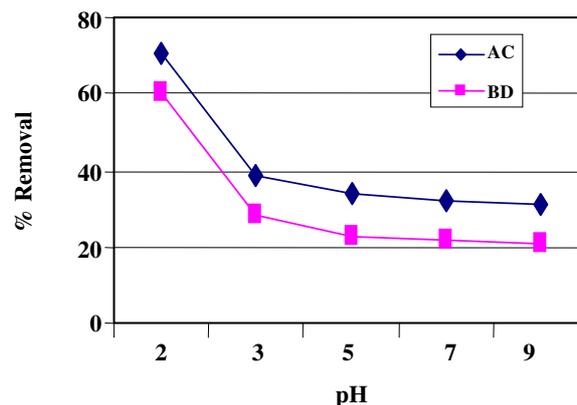


Fig. 1: Effect of pH on sorption of 0.2 mmol/L Cr(VI) after 60 min by AC and BD prepared from *Sargassum* sp. In the figure removal Cr(VI) firstly decreased and then with increase.

$$dq_t/dt = K_2 (q_e - q_t)^2 \quad (6)$$

Where  $K_2$  is the equilibrium rate constant (g/mg.min), and  $Q_e$  and  $q_t$  are the sorption capacities at equilibrium at time  $t$ .

The integrated form of Eq. (5) becomes

$$1/(q_e - q_t) = 1/(q_e) + K_2 t \quad (7)$$

which has the linear form:

$$1/q_t = 1/K_2 q_e^2 + (1/q_e) t \quad (8)$$

A plot  $t/q_t$  versus  $t$  shows a straight line of slope  $(1/q_e)$  and an intercept of  $(1/K_2 q_e^2)$  [22].

## RESULTS AND DISCUSSION

The present study shows that AC and BD prepared from brown algae *Sargassum* have an ability to remove Cr(VI) from contaminated water. The data obtained from this work supports the view that the AC is an effective and low-cost adsorbent for the removal of Cr(VI) from aqueous solutions. The adsorption of metal ions is dependent on AC, the concentration of metal ions, retention time, and the pH of the metal solution.

### Effect of pH on adsorption

The initial pH of the metal solution is an important parameter affecting adsorption of metal ions [23]. The effect of initial pH on the removal of Cr(VI) using AC and BD prepared from *Sargassum* were studied (Fig. 1).

It is clear that the removal of Cr(VI) decreased with an increase in pH from 1.0 to 9.0, and an optimum pH of about 2.0 was observed. With this test, we appointed pH 2 in all examination. In previous literature, similar observations have been reported for filtration at different pH [24]. In the figure, the removal Cr(VI) firstly decreased with an increase in pH from 1.0 to 9.0, and an optimum pH of about 2.0 was observed; AC (78%), and BD (60%) prepared. Adsorption of Cr(VI) below pH 3.0 suggests that binding of the oxidation state of chromium occurred through electrostatic attraction to the positively charged functional groups on the surface of the sorbent cell wall due to the presence of more functional groups carrying positive charge at pH < 3, while at pH > 3 the sorbent cell wall possesses more groups carrying a net negative charge that repulses the metal anions. There was a removal at pH > 3.0, but the rate of removal was reduced, which could be considered to be due to the presence of physical adsorption on the surface of the sorbent [25].

At low pH, on the other hand, Cr(VI) had a higher redox potential and favored Cr(VI) bioreduction [26]. In addition, reductions in the biomass such as carbohydrate and protein could supply electrons for Cr(VI) bioreduction, with partial release of soluble organics or the final oxidized product [27]. Acidic pH biomass contains the positive oxidation state of chromium due to protonation and Chromium remains in the anionic form (i.e.  $\text{HCrO}_4^-$  or  $\text{Cr}_2\text{O}_7^{2-}$ ), hence sorbed optimally onto the active sites of the biomass.

#### Effect of retention time

Results indicate that removal efficiency increased with an increase in contact time before equilibrium was reached. Other parameters such as dose of adsorbent, pH of solution, and initial concentration were kept optimum, while temperature was kept at 25° C. It can be seen that  $\text{Cr}^{6+}$  removal efficiency increased when contact time was increased from 15 to 120 min. Optimum contact time for both dried and activated carbon biosorbent was found to be 120 min. In previous research, similar findings have been reported by the evaluation of the marine algae *Gracilaria corticata* for the adsorption of heavy metals from wastewater in a packed column [28].

#### Effects of biosorbent dose

The dependence of Cr(VI) sorption on dose was studied

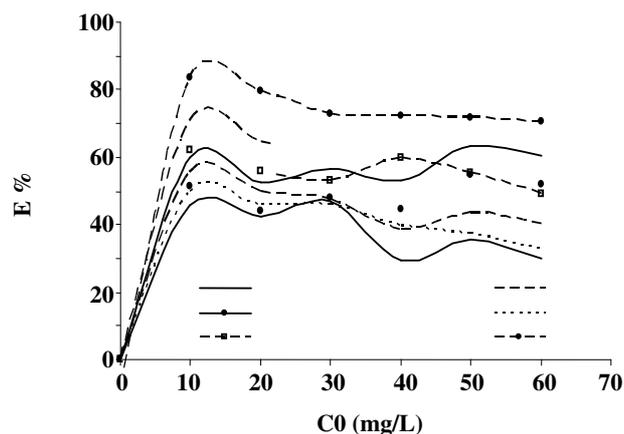


Fig. 2: Effect on Cr(VI) of initial concentration of solution uptake prepared from *Sargassum sp.* by AC and BD.

by varying the amount of adsorbents from 0.4 to 0.8 g while keeping other parameters (pH, initial concentration, and contact time) constant. From the results it can be observed that removal efficiency of the adsorbent generally improved with increasing dose (in the units of g) [29]. Biosorption rapidly occurred onto the algae biosorbent and 120 min were necessary to reach the sorption equilibrium and 0.6g of biosorbent showed higher uptake.

#### Effect of metal Ion concentration

The initial concentration of metal ions provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases [30]. Fig. 2 represents the effect of different initial concentrations of Cr(VI) 0.2–1.2 mmol/L on biosorption of Cr(VI) using dried *Sargassum* and its AC. The maximum adsorption capacity was found to be 3.69 and 6.877 mg/g for BD and the AC developed from it, respectively.

#### Adsorption isotherm

Adsorption equilibrium isotherms were studied using MD dosages of 0.2, 0.4, 0.7 and 1.0; and AC dosages of 0.2, 0.4, 0.7 and 1.0 per 100mL of aqueous Cr(VI). Solutions of initial concentrations ranged from 0.1 to 1.1 mmol/L for algae and 0.1–5.3 mmol/L for MD and AC using initial pH 5.0. For these experiments, the screw-cap conical flasks were shaken at a speed of 200 rpm and room temperature ( $25 \pm 2^\circ \text{C}$ ) for the required contact time. Then, the solution was filtered through a  $0.45 \mu\text{m}$  membrane filter. The  $\text{Ni}^{2+}$  uptake was calculated by the

Table 2: Parameters of kinetic models for biosorption of Cr(VI).

Parameter		First-order kinetic model			Second-order kinetic model		
Algae	Initial Cr(VI) concentration ( mmol/L )	K <sub>2</sub>	q <sub>e</sub> (calculated )	R <sup>2</sup>	K <sub>2</sub>	q <sub>e</sub> (calculated )	R <sup>2</sup>
AC	0.6	0.00	0.04	0.67	0.057	1.00	1.00
	1.1	0.07	0.03	0.68	0.014	1.03	0.99
	1.5	0.05	0.02	0.76	0.007	1.08	0.99
BD	0.6	0.01	0.15	0.92	0.003	0.99	1.00
	1.1	0.00	0.03	0.98	0.065	0.84	1.00
	1.5	0.00	0.02	0.91	0.004	0.91	1.00

simple concentration difference method. Adsorption isotherms are important for describing how an adsorbate will interact with an adsorbent and are critical in the use of adsorbents. Equilibrium studies on adsorption isotherms are characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The equilibrium between adsorbent and adsorbate is described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature ( $23 \pm 2^\circ\text{C}$ ), at equilibrium. To study the adsorption isotherm, two models were analyzed.

#### Langmuir and Freundlich isotherms

The Langmuir adsorption isotherm is the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent.

The applicability of the empirical Freundlich isotherm was also analyzed based on the sorption on a heterogeneous surface, using the same set of experimental data of dried brown algae and its activated carbon. The isotherm experimental results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherms. The Langmuir constant ( $q_{\max}$ ) is dependent on experimental conditions such as solution pH. Another importance in evaluating sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant (b). As we can see from Table 1, data could be well modeled according to either the Langmuir or Freundlich adsorption isotherm. In previous investigations,

a similar method using the marine algae *Gracilaria* for the biosorption of Ni(II) was reported [31].

#### Kinetic modeling

The Lagergren first-order rate constant ( $k_{1,\text{ads}}$ ) and  $q_e$  determined from the model indicated that this model failed to estimate  $q_e$  since the experimental values of  $q_e$  differed from those estimated in Table 2. Subsequently, the rate of uptake of Cr(VI) onto the biomass increased quickly to 120 min, and no further adsorption was observed beyond this period. The Cr(VI) uptake by the biosorbents was best described by the pseudo second-order rate model.

The pseudo second-order model is based on the supposition that adsorption follows a second order, which means the rate of occupation of adsorption sites is proportional to the squares of the number of unoccupied sites [32].

In previous literature for the evaluation of the AC prepared from the algae *Gracilaria* for the adsorption of Cu(II) the adsorption has been reported to follow the second-order rate expression [33].

The variation in rate should be proportional to the first power of concentration for strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process. It was observed that the kinetic model fits well for the first 40 min and thereafter the data deviate from the theory. Thus, the model shows the initial stages where rapid adsorption occurs well but cannot be applied for the entire adsorption process. *Ho & McKay* reported that the sorption data were represented well by the Lagergren second-order model only for the rapid initial phase that occurs for a contact time of 0–30 min.

This confirms that it is not appropriate to use the Lagergren kinetic model to predict the adsorption kinetics for chromium onto dried green algae and its activated carbon for the entire sorption period. While it gave predicted  $q_e$  far from the experimental  $q_e$  for both dried green algae and activated carbon, which shows that the pseudo second-order model can be applied but is not appropriate to describe the entire process and to predict the  $q_e$ .

As a result of failure in applicability of the pseudo second-order, the adsorption kinetics was explained by *Ho & McKay*. The second order rate constants  $K_2$ , the calculated  $q_e$  values and correlation coefficients were reported in Table 2. It was observed that the pseudo second-order rate constant ( $K_2$ ) decreased with increased initial concentration. The calculated  $q_e$  values agree very well with the experimental values and the regression coefficients were above 0.99 and 1.0, which shows that the pseudo second-order model can be applied for the entire adsorption process and confirms the adsorption of Cr(VI) onto BD and its AC.

#### Adsorption equilibrium

The isotherm experimental results showed that the data could be well modeled according to the Langmuir and Freundlich adsorption isotherms. The Langmuir constant ( $q_{max}$ ) is dependent on experimental conditions such as solution pH. Another important factor in evaluating sorbent performance is the initial gradient of the adsorption isotherm, since it indicates the sorbent affinity at low metal concentrations. In the Langmuir equation, this initial gradient corresponds to the affinity constant (b). The Freundlich and Langmuir isotherm constants were obtained and are presented in Table 1.

#### CONCLUSIONS

The batch removal of toxic hexavalent chromium ions from wastewater and aqueous solution using dried brown algae *Sargassum* sp. and its activated carbon were examined. Batch equilibrium sorption experiments were carried AC and BD as biosorbent, optima conditions were established at pH of 2.0,  $Cr^{6+}$  concentration at 3.69 BD and 6.877 mg/g AC and equilibrium time of 120 min. The adsorption was in the range of 83.55% and 91.98%, respectively.

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