

## **O 1. BIOCHAR PRODUCED FROM PYROLYSIS OF OLIVE POMACE AS AN ADSORBENT FOR CR (VI) REMOVAL FROM AQUEOUS SOLUTIONS**

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**ABSTRACT:** In this study, utilization of biochar obtained from pyrolysis of olive pomace as an adsorbent for removal of Cr (VI) from aqueous solution under different conditions. The adsorption experiments were implemented in batch process. The effects of various process parameters were investigated on the adsorption efficiency. The optimum removal conditions were determined as pH 3, time 30 min, concentration 10 mg L<sup>-1</sup>, dose 0.4 g and temperature 30 °C. The properties of biochar before and after adsorption were examined with Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses. The adsorption performance of biochar was evaluated by Langmuir and Freundlich isotherm models by using different concentrations of Cr (VI) in the range of 10-80 mg L<sup>-1</sup>. Langmuir isotherm fitted to experimental data with higher accuracy and a maximum adsorption capacity of 4.9 mg g<sup>-1</sup>. The pseudo second order kinetic model gave a better fit with best correlation to the kinetic data. In the light of the results, it can be said that the biochar was successfully used as a low-cost and environmental friendly adsorbent for Cr (VI) removal from contaminated water.

*Keywords: Olive pomace, pyrolysis, biochar, adsorption, Cr (VI)*

### **1. INTRODUCTION**

With rapid industrialization and economic development, the discharge of heavy metals to water has become one of the worldwide problems that threaten human health and ecosystem (Basha et al., 2008; Ibrahim et al., 2010). Heavy metals are very toxic even at very low concentrations, because they are non-biodegradable materials and have tendency to accumulate in living organisms (Fu & Wang, 2011). Chromium (Cr) which exists in two forms of III and VI is one of these toxic metals. Cr (VI) is more hazardous than Cr (III) due to its toxicity and carcinogenic properties (Hu et al., 2011).

Cr (VI) was classified as one of the top 16<sup>th</sup> hazardous substances by the agency for Toxic Substances and Disease Registry (ATSDR) (Jain et al., 2010). In many countries, the permissible limit of Cr (VI) to be discharge to surface water from industrial effluents varies from 0.05 to 0.1 mg L<sup>-1</sup> (Bansal et al., 2009). So, the removal of Cr (VI) from wastewater originated in leather tanning, cooling tower, plating, electroplating etc, is very important (Owlad et al., 2009). Various techniques such as flotation (Rubio et al., 2002), ultrafiltration, membrane (Landaburu-Aguirre et al., 2010), reverse osmosis (Benito & Ruiz, 2002), chemical precipitation, ion exchange, coagulation, flocculation (Fu & Wang, 2011), photocatalysis (Yoon et al., 2009) and adsorption are used to remove heavy metals from aqueous solution. Among the treatment techniques, adsorption was considered as one of the most effective methods because of high cost and residual sludge of other techniques (Zhong et al., 2013).

The Cr (VI) removal process have been carried out using different bioadsorbents such as biochar derived from rice straw (Gao et al., 2008), maize tassel (Zvinowanda et al., 2009), sunflower waste (Jain et al., 2010), sugar beet tailing (Dong et al., 2011), oak wood, oak bark (Mohan et al., 2011), wheat straw (BCS), wicker (Tyłak et al., 2015), peanut hull (Han et al., 2016) and corn stalk (An et al., 2018).

Olive pomace as a by-product of olive production industry have been used in different adsorption processes (Pagnanelli et al., 2002; Vegliò et al., 2003; Martín-Lara et al., 2008). In this study, char obtained from pyrolysis of olive pomace was investigated as an adsorbent for Cr (VI) removal. The effects of adsorption parameters (pH, time, mass of adsorbent, initial metal concentration and temperature) on the adsorption efficiency were examined. And also, the isotherms, kinetics and thermodynamic of Cr (VI) adsorption onto the char were studied at optimum conditions.

## 2. MATERIALS AND METHOD

### 2.1. Preparation of Olive Pomace Char

Olive pomace char was obtained as solid residue after pyrolysis of olive pomace in fixed bed pyrolysis reactor. Pyrolysis process was carried out at 500 °C with a heating rate of 10 °C/min under N<sub>2</sub> gas (150 cm<sup>3</sup>/min).

### 2.2. Cr (VI) Adsorption Studies

The stock solution of Cr (VI) (1000 mg L<sup>-1</sup>) was prepared by dissolving potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>) in deionized water. The effects of pH, time, mass of adsorbent, initial Cr (VI) concentration and temperature on adsorption were studied using the experimental conditions as shown in Table 1. Cr (VI) concentration was determined with measuring absorbance of 540 nm by UV-vis spectrophotometer. The percentage removal (R, %) of Cr (VI) and adsorption capacity (q<sub>e</sub>, mg g<sup>-1</sup>) were calculated using the following equations:

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentration of Cr (VI) (mg L<sup>-1</sup>), respectively. V is the volume of Cr (VI) solution (L) and m is the mass of the adsorbent (g).

### 2.3. Characterization

The FTIR analyses were used to determine vibration frequency changes in functional groups of char before and after Cr (VI) adsorption. The morphology and elemental composition of the char were investigated by SEM analysis equipped with EDX analysis.

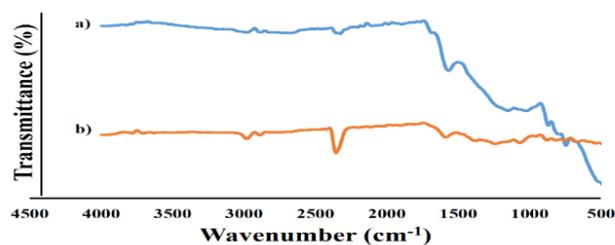
**Table 1.** Experimental Conditions for Cr (VI) Adsorption Process

	pH (A)	Time (B) (min)	Initial concentration (C) (mg L <sup>-1</sup> )	Adsorbent dose (D) (g)	Temperature (E) (°C)
Effect of A	<b>1.5-6</b>	30	20	0.1	20
Effect of B	3	<b>15-120</b>	20	0.1	20
Effect of C	3	30	<b>10-80</b>	0.1	20
Effect of D	3	30	10	<b>0.05-0.4</b>	20
Effect of E	3	30	10	0.4	<b>20-50</b>

## 3. RESULTS AND DISCUSSION

### 3.1. FTIR Analysis

The FTIR spectrum of char is shown before and after Cr (VI) adsorption in Fig. 1. The peaks at 1100 cm<sup>-1</sup> and 3641 cm<sup>-1</sup> were indication of existence of carboxyl and hydroxyl groups. These peaks a bit shifted to lower wavenumbers. It can be said that the carboxyl and hydroxyl groups could be main functional groups for Cr (VI) adsorption (Bansal et al., 2009; Gan et al., 2015; Garg et al., 2007).



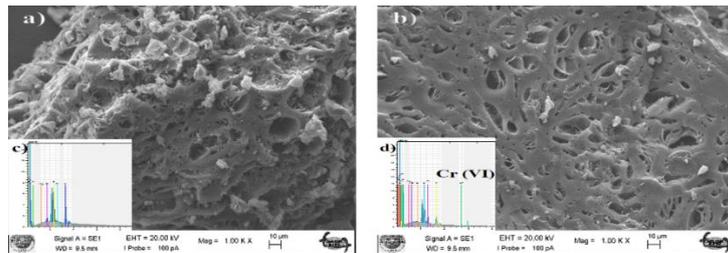
**Figure 1.** FTIR Spectrum of Char (a) Before and (b) After Adsorption of Cr (VI)

### 3.2. SEM Analysis

The SEM image of char is shown before and after Cr (VI) adsorption in Fig. 2. As seen in Fig. 2a, the surface of char was rough before Cr (VI) removal. However, it was observed that the surface of char was smooth after Cr (VI) removal (Fig. 2b).

### 3.3. EDX Analysis

The EDX spectrum of char is shown before and after Cr (VI) adsorption in Fig. 2c-d. A reduction in intensity of C peak was clearly seen after Cr (VI) removal when compared to the fresh one. Also, the strong peak of Cr (VI) component was determined in the EDX spectrum of char in case of Cr (VI) adsorption.



**Figure 2.** SEM Image of Char (a) Before And (b) After Adsorption of Cr (VI). Inserts show EDX Spectra of Char

### 3.4. Effect of Experimental Parameters on Cr (VI) Removal

#### 3.4.1. The effect of pH

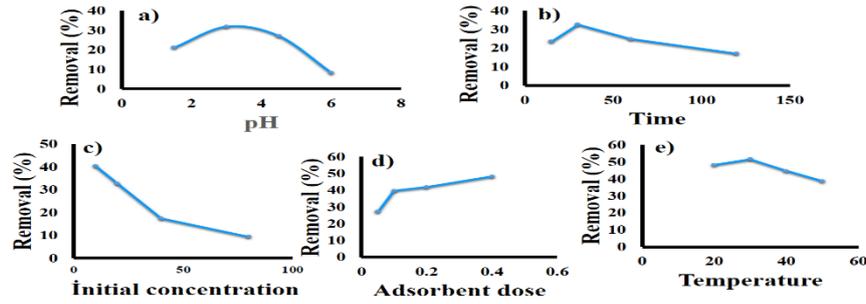
Different experiments were carried out by varying pH from 1.5 to 6, while the other parameters were kept constant in order to explain the effect of pH of the solution on the adsorption of Cr (VI). Removal of Cr (VI) at different pH values is shown in Fig. 3a. It was observed that removal of Cr (VI) increased with increase pH until pH 3. And then, Cr (VI) removal considerably decreased. It can be said that the increase of Cr (VI) removal at low pH values is due to presence a lots of H<sup>+</sup> ions. H<sup>+</sup> ions scattered in solution made a neutralization with negatively charged hydroxyl ions which cause a hindrance to diffusion of the positively charged dichromate ions (Dubey & Gopal, 2007). In the highly pH, the H<sup>+</sup> ions decrease which lead decreasing Cr (VI) adsorption (Selvi et al., 2001).

#### 3.4.2. The effect of time

Removal of Cr (VI) as a function of time is shown in Fig. 3b. Maximum removal of Cr (VI) was determined in 30 min due to more available sites of adsorbent at beginning of adsorption. As the available adsorption sites become to decrease, percentage removal of many substances usually decreases in adsorption processes (Bulut, 2007).

#### 3.4.3. The effect of initial concentration

The effect of initial concentration on removal of Cr (VI) is shown in Fig. 3c. It was observed that removal of Cr (VI) decreased with increasing initial concentration. During the adsorption, a decrease in the number of active vacant sites on the surface of adsorbent causes to reduce percentage removal (Gupta & Balomajumder, 2015). In spite of a decrease in Cr (VI) removal, adsorption capacity increased. As the initial concentration increase from 10 to 80 ppm, the adsorption capacity increased from 2.019 to 3.678 mg g<sup>-1</sup>, respectively. It could be attributed to the greater mass driving force which works to overcome the transfer limitation (Agarwal et al. 2013).



**Figure 3.** The Effect of Parameters on the Adsorption of Cr (VI) (a) pH, (b) Time, (c) Initial Concentration, (d) Adsorbent Dose and (e) Temperature

### 3.4.4. The effect of adsorbent dose

The effect of adsorbent dose on removal of Cr (VI) is shown in Fig. 3d. It was clearly seen that removal of Cr (VI) significantly increased with amount of adsorbent dose. High surface area exposed to adsorption and availability of more adsorption sites generally have synergistic effects on the adsorption process (Garg et al., 2007).

### 3.4.5. The effect of temperature

The effect of temperature on removal of Cr (VI) is shown in Fig. 3e. The removal of Cr (VI) demonstrated an increase with increasing temperature from 20 to 30 °C. It can be attributed to a decrease in solution viscosity, in other words, helps to increase rate of adsorbed Cr (VI) molecules within the pores (Agarwal et al. 2013). However, the removal of Cr (VI) decreased above 30 °C which is probably due to tendency of desorption. And also, it was stated that the adsorption process of Cr (VI) was exothermic process (Saltalı et al., 2007).

## 3.5. Adsorption Isotherms

The isotherm adsorption data was represented by Langmuir and Freundlich isotherm models, respectively (SenthilKumar et al., 2011).

### 3.5.1. Freundlich isotherm model

Freundlich isotherm model describes adsorption on the heterogeneous surface with uniform energy (Foo & Hameed, 2010). Freundlich isotherm equation is given as:

$$\log_{10} q_e = \log_{10} K_f + \frac{1}{n} \log_{10} C_e \quad (3)$$

where  $q_e$  is adsorption capacity ( $\text{mg g}^{-1}$ ),  $C_e$  is equilibrium concentration of Cr (VI) ( $\text{mg L}^{-1}$ ).  $K_f$  ( $\text{l g}^{-1}$ ) and  $n$  are Freundlich constants which related to adsorption capacity and adsorption intensity.

### 3.5.2. Langmuir isotherm model

Langmuir model assumes monolayer adsorption without interaction and steric hindrance between adsorbed molecules (Bansal et al., 2009). Langmuir isotherm equation is given as:

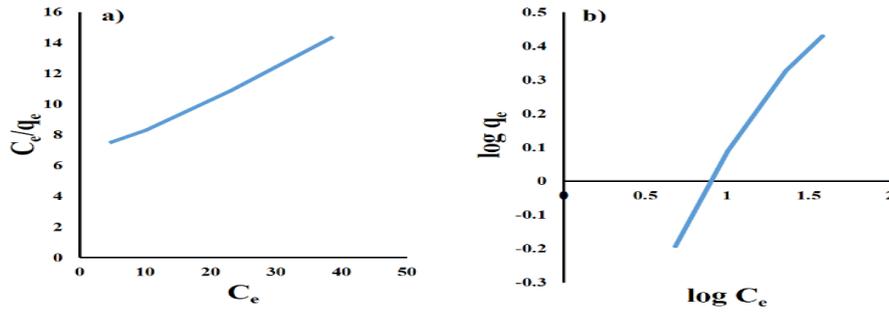
$$\frac{C_e}{q_e} = \frac{1}{Q_m \cdot b} + \frac{C_e}{Q_m} \quad (4) \quad \text{where}$$

$Q_m$  ( $\text{mg g}^{-1}$ ) and  $b$  ( $\text{L mg}^{-1}$ ) are Langmuir constants related with adsorption capacity and adsorption rate, respectively. A dimensionless constant, commonly known as separation factor ( $R_L$ ) is represented as:

$$R_L = \frac{1}{(1+b \cdot C_0)} \quad (5)$$

The value of  $R_L$  indicates unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), irreversible ( $R_L = 0$ ) or favorable ( $0 < R_L < 1$ ) processes (Foo & Hameed, 2010).

Langmuir and Freundlich isotherms are shown in Fig. 4. And also, isotherm parameters are given in Table 2. When compared to correlation coefficients ( $R^2$ ), it was deduced that Langmuir isotherm model was well fitted the experimental data. The maximum adsorption capacity of Cr (VI) was determined as  $4.9 \text{ mg g}^{-1}$ . The adsorption process was favorable according to  $R_L$ .



**Figure 4.** (a) Langmuir and (b) Freundlich Isotherms at Optimum Conditions (pH 3, time 30 min, initial concentration 10 ppm, adsorbent dose 0.4 g and temperature 30 °C)

**Table 2.** Langmuir and Freundlich Isotherm Parameters

Langmuir model			Freundlich model			
$Q_m$ (mg g <sup>-1</sup> )	$b$ (l mg <sup>-1</sup> )	$R^2$	$R_L$	$K_f$ (l g <sup>-1</sup> )	$n$	$R^2$
4.9	0.032	0.996	0.757	0.229	1.443	0.987

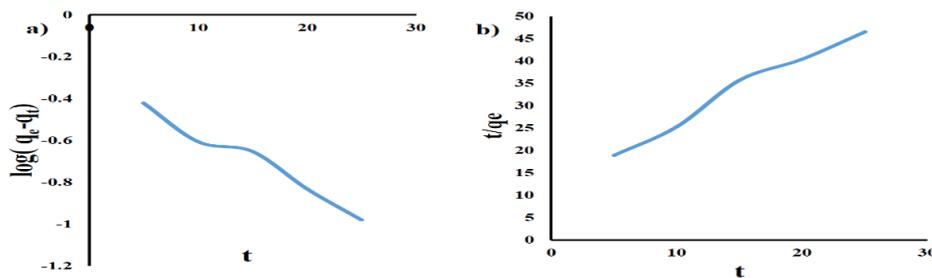
### 3.6. Adsorption Kinetics

The kinetics are used to explain the mechanism of adsorption process. The kinetic models are pseudo first order and pseudo second order were utilized to simulate the experimental kinetic data. The pseudo first and second order of the equations is given as, respectively:

$$\log_{10} (q_e - q_t) = \log_{10} q_{ecal} - k_1 \cdot t \tag{6}$$

$$\frac{t}{q_e} = \frac{1}{k_2 \cdot q_{ecal}^2} + \frac{t}{q_{ecal}} \tag{7}$$

where  $k_1$  (min<sup>-1</sup>) and  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) are the pseudo first order and pseudo second order reacted rate constants, respectively (Chakravarty et al., 2010). Fig. 5 shows the kinetic models and kinetic parameters are presented in Table 3. As per  $R^2$  values, it was observed that the pseudo second order is more fitted the experimental data than the pseudo first order. The chemisorption of Cr (VI) on char was rate limiting mechanism in this process and it can be said that Cr (VI) ions were onto the surface of char by chemical interaction (Gan et al., 2015).



**Figure 5.** (a) Pseudo-First Order and (b) Pseudo-Second Order Kinetic Model

**Table 3.** Kinetic Parameters

Pseudo-First order			Pseudo-Second order		
$q_{ecal}$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$	$q_{ecal}$ (mg g <sup>-1</sup> )	$k_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$R^2$
0.5049	0.0268	0.9778	0.7117	0.1606	0.9850

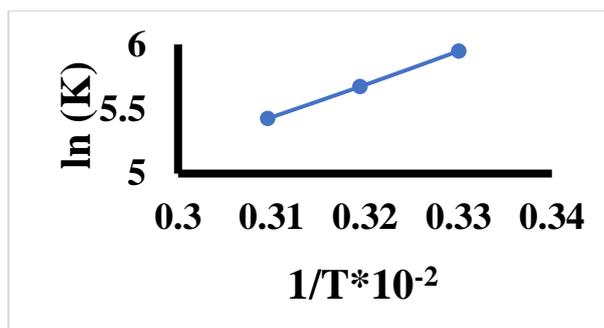
### 3.7. Adsorption Thermodynamics

The parameters of thermodynamics (Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ )) were calculated by given equations:

$$\Delta G^{\circ} = -RT \ln(K) \quad (8)$$

$$\ln(K) = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (9)$$

K was calculated by  $K = 55.5 \times q_e / C_e \times M_{\text{adsorbate}}$ . 55.5 was the concentration of water and  $M_{\text{adsorbate}}$  was the molecular weight of adsorbate (Anastopoulos & Kyzas, 2016). The entropy and the enthalpy were calculated from the intercept and slope, respectively from the Fig. 6. And also, thermodynamic parameters are given in Table 4. The negative values of  $\Delta G^{\circ}$  indicate the spontaneous adsorption process and the negative value of  $\Delta H^{\circ}$  confirms the exothermic nature of process. Moreover, a negative value of  $\Delta S^{\circ}$  indicates the decrease of randomness.



**Figure 6.** lnK as a function of 1/T

**Table 4.** Thermodynamic Parameters

T (°C)	ln (K)	$\Delta G^{\circ}$ (cal mol <sup>-1</sup> )	$\Delta H^{\circ}$ (cal mol <sup>-1</sup> )	$\Delta S^{\circ}$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
30	5.948994202	-3576.697	-5075.3101	-4.949707
40	5.673216563	-3523.463		
50	5.426428173	-3477.864		

#### 4. CONCLUSION

In this study, Cr (VI) adsorption from aqueous solution using olive pomace char as an alternative adsorbent was successfully carried out. The maximum removal efficiency was determined as 51.52% with a maximum adsorption capacity 4.9 mg g<sup>-1</sup> at optimum condition (pH 3, time 30 min, initial Cr (VI) concentration 10 mg L<sup>-1</sup>, amount of adsorbent 0.4 g and temperature 30 °C). The results showed that the low-cost olive pomace char can be potentially applied in environmental fields. And also, usage of this char provided to decrease waste accumulation which limits environmental pollution.

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