Biochar Produced from Co-Pyrolysis of Olive Pomace & Crude Oil as an Adsorbent for Cr (VI) Removal from Aqueous Solutions

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ABSTRACT: *This study investigated aqueous solution treatment to remove Cr (VI) using a biochar-based adsorbent. Olive pomace and crude oil were used to synthesize the biochar adsorbent via co-pyrolysis for the first time. The biochar properties were examined with Fourier Transform Infra-Red (FT-IR) spectroscopy, scanning electron microscopy (SEM), and Energy Dispersive X-ray (EDX) analyses before and after adsorption. The adsorption experiments were carried out in a batch process under different experimental conditions. The optimum adsorption efficiency was experimentally found to be at pH of 1.5, contact time of 15 min, Cr (VI) initial concentration of 20 mg/L, adsorbent dose of 0.4 g, and 303 K. Langmuir and Freundlich isotherms were used to evaluating the adsorption performance of biochar, and the Langmuir isotherm model was well fitted to experimental data with a maximum adsorption capacity of 9 mg/g. Kinetic experimental data was best described using a pseudo-second-order kinetic model. The thermodynamic parameters of the adsorption process were examined in detail, and the process was exothermic and spontaneous in nature. It is concluded that biochar can be successfully used as an adsorbent for the treatment of Cr (VI) contaminated water. Additionally, the evaluation of olive pomace provided not only a decrease in waste accumulation in the olive production industry but also the synthesis of an inexpensive and environmentally friendly adsorbent.*

KEYWORDS: *Adsorption; Chromium (VI); Biochar; Olive pomace; Co-pyrolysis.*

INTRODUCTION

Due to their technological importance, heavy metals are extensively used in many industries. Proper treatment of the wastewater from these industries provides a significant contribution to the environment and human health. Insufficient treatment of wastewater polluted by heavy metals causes many environmental problems.

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Heavy metals, even at very low concentrations, are very toxic due to their non-biodegradable nature and their accumulation in living organisms [1, 2]. In fact, in case of their presence at higher concentrations inside living organisms, heavy metals pose serious problems for living organisms and adversely affect human health as well. For example, cadmium (II), copper (II), and nickel (II) ions can cause kidney disease, liver disease, dermatitis, or chronic asthma [3, 4].

Chromium is available in two forms: (1) hexavalent (VI), which is higher in toxicity, and (2) trivalent (III) [3]. According to the standards of drinking water by the World Health Organization (WHO), chromium concentration in water should be lower than 0.05 mg/L [5]. High exposure to Cr (VI) can lead to nausea, vomiting, epigastric pain, severe diarrhea, hemorrhage, and digestive tract and lung cancers [6]. The Agency for Toxic Substances and Disease Registry (ATSDR) classified Cr (VI) as one of the most hazardous 16 substances in the world [7], so Cr (VI) must be purified from wastewater before disposal.

Different separation and purification techniques have been utilized to treat Cr (VI) polluted wastewater such as flotation [8], reverse osmosis [9], photocatalysis [10], ultrafiltration membrane [11], coagulation, flocculation, chemical precipitation, ion exchange, and adsorption [1] which is an effective and economically feasible method for the treatment of heavy metals from wastewater [12]. The adsorption process is flexible and produces high-quality treated water in many cases. In addition, some cases of adsorption processes are reversible and adsorbents can be regenerated by an appropriate desorption process [13].

Activated carbon is an effective adsorbent for the adsorption of Cr (VI). However, because of its high cost and difficulty to regenerate, alternative material is required which is inexpensive, more available in nature, and easy to regenerate; or non-regenerable from inexpensive abundant sources such as waste from industrial and agricultural operations. Biochar from these materials is synthesized by pyrolysis which is a thermal decomposition in the presence of no or low oxygen [14, 15]. The formed solid char is mainly composed of a carbon-rich matrix containing the inorganic compounds that are present in the raw wastes. Many times, the preparation of these materials includes physical or chemical activation that makes the materials oxygenated or hydrophilic. The chemical activation which is generally conducted by H_2SO_4, H_3PO_4, KOH, NaOH, and $ZnCl_2$ has many advantages compared to physical activation. The chemical activation provides high surface area, high efficiency, low-temperature process, and operation in a short time [16-19]. Cr (VI) removal process has been carried out using different biochars derived from oily seeds of Pistacia terebinthus L. [20], wheat bran [21], oak wood and bark [22], and pineapple [23]. Olive pomace, a by-product of the olive production industry, has been used in different adsorption processes [24, 25].

Treating and disposing of the waste resulting from the production of olive oil are considered to be an environmental issue that must be solved [26]. Olive waste has been used as an adsorbent for the treatment of many heavy metals leading to a decrease in waste accumulation. Olive waste contains several functional groups such as carboxylic, hydroxyl, methoxy, and phenolic groups which are potentially active in metal removal from aqueous solutions [27]. The aim of the study was the utilization of by-products of the olive production industry resulting in the limitation of waste accumulation and production of low-cost materials as an adsorbent for wastewater treatment. Therefore, in this study, biochar was produced from the co-pyrolysis of olive pomace with crude oil and it was evaluated as an adsorbent for Cr (VI) removal process for the first time. The effects of adsorption parameters (pH, contact time, adsorbent dose, initial metal ion concentration and temperature) on the adsorption efficiency were examined. Furthermore, the Cr (VI) adsorption isotherms, kinetics and thermodynamic were studied at optimum experimental conditions.

EXPERIMENTAL SECTION

Materials

In this study, byproducts of olive oil factories in the Hatay-Turkey region were used to obtain biochar. Potassium dichromate ($K_2Cr_2O_7$) supplied by Merck was used as a Cr (VI) source. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased to adjust pH of the solutions from Sigma-Aldrich. For the preparation of Cr (VI) solution in adsorption experiments, deionized water was used.

Preparation of Biochar

Co-pyrolysis of olive pomace with crude oil was performed at 773 K with a heating rate of 283 K/min under 150 cm^3/min

Table 1: Experimental conditions for Cr (VI) adsorption.

	pH (A)	Contact time(B) (min)	Initial concentration (C) (mg/L)	Adsorbent dose (D) (g)	Temperature (E) (K)
Effect of A	1.5-6	30	20	0.1	293
Effect of B	3	15-120	20	0.1	293
Effect of C	3	30	10-80	0.1	293
Effect of D	3	30	10	0.05-0.4	293
Effect of E	3	30	10	0.4	293-323

nitrogen gas flow rate in a fixed bed pyrolysis system [28, 29]. The co-pyrolysis product was modified using 1 M HCl at 373 K for 24 h. The modified biochar was washed with distilled water until a stable pH, and then oven-dried at 333 K for 12 h.

Cr (VI) Adsorption Experiments

Solid $K_2Cr_2O_7$ was used to prepare the standard stock solution. The solution was prepared by dissolving 2.828 g of $K_2Cr_2O_7$ in 1000 mL of deionized water for the stock solution of 1000 mg/L Cr (VI). In order to prepare solutions with different concentrations, standard Cr (VI) stock solution was diluted. pH of the solutions was adjusted with 0.25 M NaOH and 0.25 M HCl.

Cr (VI) concentration in the samples was determined using a UV-Vis spectrometer. Shimadzu UV-1800 spectrophotometer was used to measure absorbance at 540 nm by colorimetric detection of chromium ions complexed with 1-5-diphenyl carbazide.

Batch studies were performed by adding specific quantities of adsorbent in conical flasks with a volume of 250 mL at 293 K under continuous agitation of 60 rpm in a water bath. The effects of pH, contact time, amount of adsorbent, initial concentration of Cr (VI), and temperature on the adsorption process were investigated using the experimental conditions shown in Table 1. Chromium concentration was measured over a fixed period to determine the adsorption capacity of the biochar. The adsorbent capacity (q_e, mg/g) and percentage Cr (VI) removal (R, %) were calculated using in there there is no reference. It should be Eqs (1) and (2).

$$q_e = (C_o - C_e) \times V / m \quad (1)$$

$$R = (C_o - C_e) \times 100 / C_o \quad (2)$$

Where C_o (mg/L) is the initial Cr (VI) concentration, and C_e (mg/L) is the equilibrium Cr (VI) concentration. m (g) is the adsorbent dose and V (L) indicates the Cr (VI) solution volume.

Characterizations

Fourier Transform Infra-Red (FT-IR) spectroscopy analysis was performed to determine functional groups belonging to biochar before and after Cr (VI) adsorption by Bruker Vertex 70 within a range of 4000 cm^{-1} - 400 cm^{-1} with a resolution of 2 cm^{-1}. The surface morphology of biochar before and after Cr(VI) adsorption was investigated by Scanning Electron Microscopy (SEM) analysis under generated voltage of 20 kV. SEM analysis was conducted by SM Zeiss LS-10 scanning electron microscope, after coating the biochar surface with a gold layer. Energy Dispersive X-ray (EDX) spectroscopy analysis was carried out to identify the elemental composition of biochar before and after Cr (VI) adsorption by EDX detectors equipped with SEM.

RESULTS AND DISCUSSION

Characterization of Biochar

FT-IR analysis

The FT-IR spectrum of biochar before and after Cr (VI) adsorption is shown in Fig. 1. The broadband with small intensity at 3711 cm^{-1} was attributed to O-H stretching vibrations of hydroxyl groups. It was seen that the band shifted to 3690 cm^{-1} due to the complexation of hydroxyl groups with Cr (VI) after adsorption [30]. At approximately 2989 cm^{-1} and 2890 cm^{-1}, the peaks related to C-H stretching vibrations were observed [31]. After Cr (VI) adsorption, the peaks with higher intensity shifted slightly [32]. The peaks at 2354 cm^{-1} and 1600 cm^{-1} contributed to the stretching of aromatic C=C ring and carbonyl groups, respectively. The small shift to 1595 cm^{-1} was explained by the complexation of carboxylic groups with Cr (VI) ions along with the adsorption process [33]. The peaks clearly appeared depending on C=O stretching

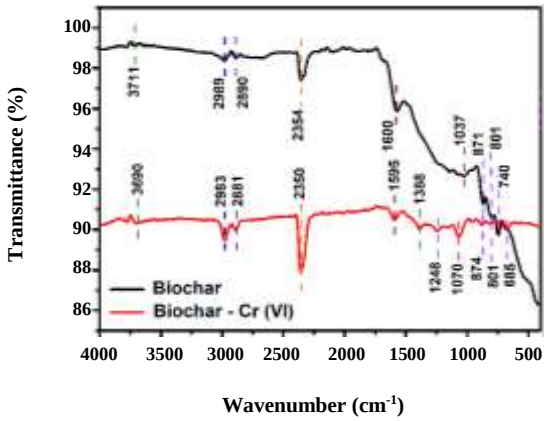

Fig. 1: FT-IR spectrum of biochar before and after Cr (VI) adsorption.

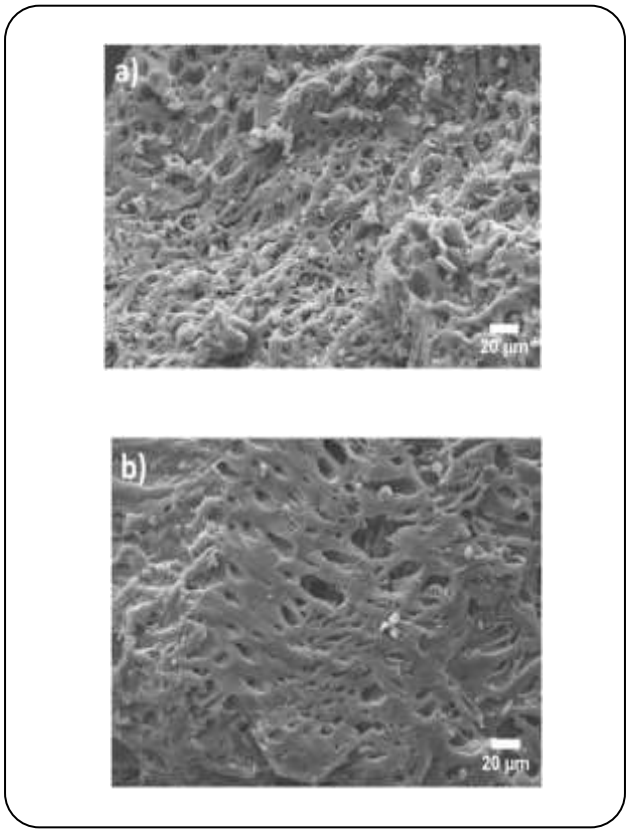

Fig. 2: SEM image of biochar a) before and b) after Cr (VI) adsorption.

of carboxyl groups and aromatic -CO stretching after Cr (VI) adsorption at 1388 cm^{-1} and 1248 cm^{-1}, respectively [34]. The peak was assigned to -CO stretching vibrations of aromatic groups at about 1037 cm^{-1}. The peaks at 871 cm^{-1}, 801 cm^{-1} and 740 cm^{-1} showed presence of adjacent H deformations [35, 36]. As a result, it can be said that Cr (VI) adsorption can be provided by functional groups on the biochar as hydroxyl and carboxyl groups.

SEM analysis

The SEM images of biochar before and after Cr (VI) adsorption are shown in Fig. 2. Similar surface morphology was obtained with that of the materials synthesized by pyrolysis in the literature [35]. As shown in Fig. 2a, the surface of biochar was rough before adsorption which provides to adsorb Cr (VI) ions easily. Effective active sites on the biochar surface led Cr (VI) adsorption depending on its surface morphology [37]. After the adsorption process, quite a smooth surface of biochar is observed in Fig. 2b. It can be explained by the accumulation of Cr (VI) ions as a layer on the biochar surface [38].

EDX analysis

The EDX spectrum of biochar before and after Cr (VI) adsorption is shown in Fig. 3. Elemental composition of biochar including high C and O content is represented before Cr (VI) adsorption in Fig. 3a. After the adsorption of Cr (VI), the intensity of C decreased considerably and the peak corresponding to Cr (VI) ions are as shown in Fig. 3b. It was a direct indication of the presence of Cr (VI) ions on the biochar surface [38].

Effect of Adsorption Parameters

Effect of pH

The solution pH is one of the adsorption parameters that have a significant role in controlling the adsorption capacity. It is generally attributed to the influence of pH on the adsorbent surface charge and the ionic forms of adsorbate in the solution [39, 40]. For the investigation of the effect of different pH values on the Cr (VI) adsorption, the adsorption process was performed using 0.1 g of biochar and 50 mL of 20 mg/L Cr (VI) solution for 30 min at 293 K. The maximum removal of Cr (VI) was observed at pH 1.5 with a percentage removal of 52.6% as shown in Fig. 4a. Cr (VI) removal significantly decreased to approximately 25.0% with increasing pH. It can be explained by the dominant oxyanion forms of Cr (VI) as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} at low pH values. On the other side, there was a presence of large amounts of H^+ ions at low pH which charge the adsorbent surface positively. Therefore, there is a strong electrostatic attraction that

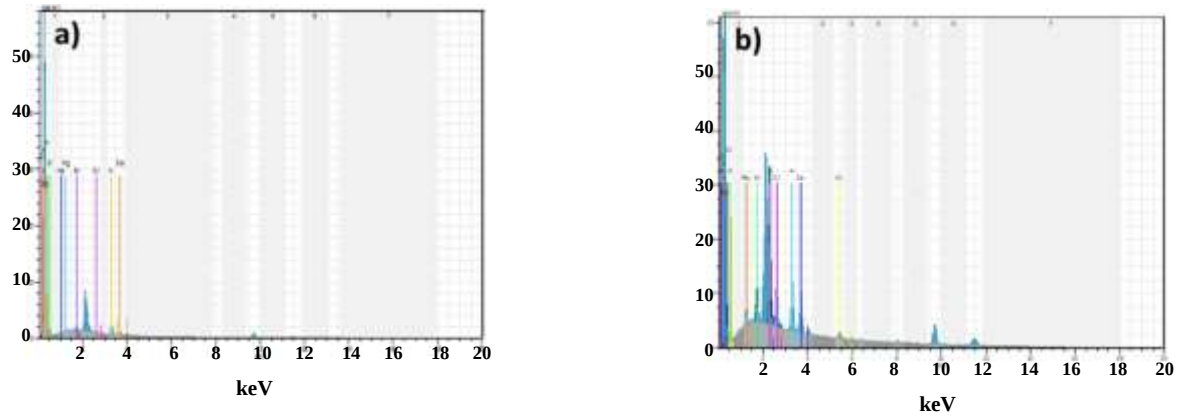

Fig. 3: EDX spectrum of biochar a) before and b) after Cr (VI) adsorption.

binds the oxyanions and the positively charged adsorbent leading to higher adsorption capacity. However, an increase in pH values leads to more OH^- (alkali ions) which hinders to adsorption of the negatively charged forms of Cr (VI). So, the adsorption capacity of Cr (VI) decreased at high pH values. Similar results have been reported regarding pH in adsorption processes in prior studies [41].

Effect of contact time

Contact time between adsorbate molecules and adsorbent is significant for adsorption processes in terms of the economy [41]. The effect of contact time on the Cr (VI) adsorption was investigated using 0.1 g of biochar and 50 mL of 20 mg/L Cr (VI) solution at pH 1.5 under 293 K. As shown in Fig. 4b, it was clear that rapid removal of Cr (VI) occurred within the initial 15 min owing to the availability of many active sites on the adsorbent surface [42]. The contact time was considerably short for an adsorption process that provides both cost and time savings. In time, the removal of Cr (VI) decreased depending on the saturation of active sites for adsorption. It can be expressed with repulsive forces between Cr (VI) ions on the biochar surface and in the solution [43]. A similar result was found using a low-cost adsorbent for the adsorption of heavy metal ions from aqueous solutions [44].

Effect of initial concentration

One of the most important parameters that have an influence on the adsorption processes is the adsorbate initial concentration. Adsorption capacity is directly proportional to the initial concentration of adsorbate in contrast to the percentage removal of adsorbate [45]. The initial concentration acts as a driving force against the resistance to mass transfer of adsorbate molecules between the aqueous phase and solid phase contributing to high adsorption capacity [46, 47]. To examine the effect of Cr (VI) initial concentration, 50 mL of Cr (VI) solutions of different concentrations were studied with 0.1 g of biochar for 15 min at pH 1.5 under 293 K. The effect of Cr (VI) solution initial concentration is shown in Fig. 4c. Maximum percentage removal of Cr (VI) was specified in the case of using 20 mg/L Cr (VI) solution. However, an increase in Cr (VI) initial concentration caused to decrease Cr (VI) removal. At high initial concentrations, complete coverage of active sites on the biochar surface led to decrease interactions between biochar and Cr (VI) ions [48, 49].

Effect of adsorbent dose

It is necessary to get the optimum adsorbent dose in order to maximize the removal of heavy metals. The effect of the adsorbent dose was investigated in the range of 0.05 - 0.4 g with 50 mL of 20 mg/L Cr (VI) solution for 15 min at pH 1.5 under 293 K. As shown in Fig. 4d, the percentage removal of Cr (VI) increased significantly with increasing adsorbent dose. It was obvious that the percentage removal of Cr (VI) reached 78.8% in the presence of 0.4 g. It can be attributed to the higher surface area of biochar [50, 51]. In many studies, a higher adsorbent dose was preferred for effective adsorption processes [52].

Effect of temperature

To examine the effect of temperature on the removal of Cr (VI), adsorption experiments were performed between

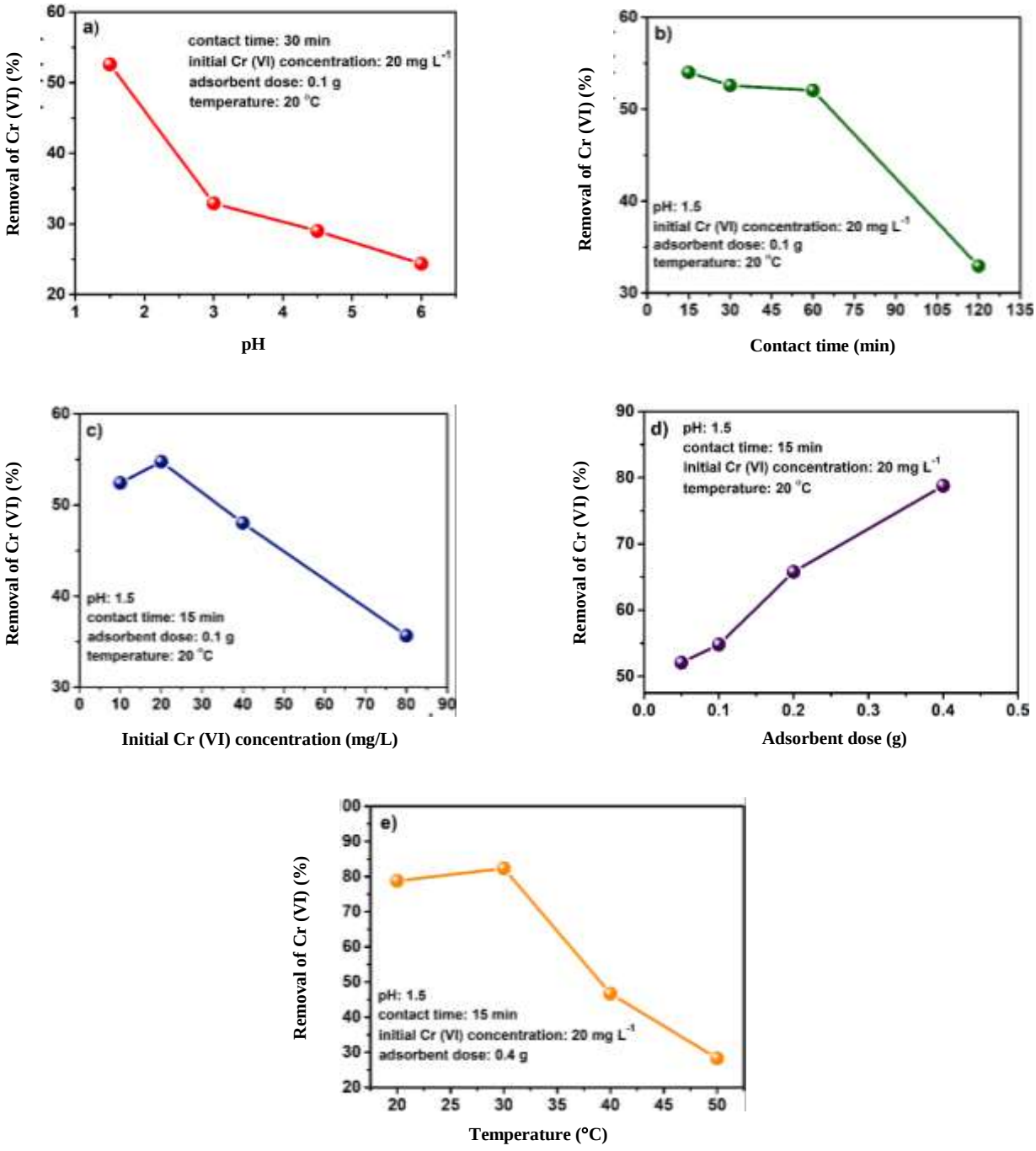

Fig. 4: Effect of a) pH, b) contact time, c) Cr (VI) initial concentration, d) adsorbent dose, and e) temperature on the removal of Cr (VI).

293 K and 323 K with 0.4 g biochar and 50 mL of 20 mg/L Cr (VI) solution for 15 min at pH 1.5. The effect of temperature on Cr (VI) removal is shown in Fig. 4e. The maximum removal of Cr (VI) was observed at 303 K with a removal percentage of 82.3%. Above 303 K, Cr (VI) removal percentage decreased depending on desorption related to increasing available thermal energy. In other words, the higher mobility of adsorbate molecules resulted in desorption at high temperatures [53]. Similar observations were reported for Cr (VI) adsorption using various adsorbents in literature studies [12, 54].

Adsorption Isotherms

The adsorption mechanism of many adsorption processes is generally described with Langmuir and Freundlich isotherm models. The Langmuir isotherm model predicts monolayer adsorption [55]. It shows that adsorption takes place on the surface in a homogeneous way with active sites which have similar energy [56]. Langmuir isotherm model is expressed by the linearized Equation (3).

$$C_e/q_e = (1/q_{max})C_e + 1/b\,q_{max} \quad (3)$$

Where q_{max} (mg/g) is the maximum adsorption capacity and b (L/mg) is the Langmuir constant. The applicability of Langmuir isotherm is evaluated with a dimensionless separation factor (R_L) that can be defined by Eq. (4) [57]. The R_L value shows how adsorption occurs: irreversible (R_L = 0), favorable (0 <R_L <1), linear (R_L = 1) or unfavorable (R_L> 1) [58].

$$R_L = 1/(1 + bC_o) \quad (4)$$

The Freundlich isotherm model shows that adsorption takes place on energetically heterogeneous and multilayer surfaces. In other words, the adsorbent surface has active sites with different energies that lead to a heterogeneous adsorption surface [59]. Freundlich isotherm model is expressed by the linearized Equation (5).

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

Where K_f (mg/g) and n are adsorption capacity and Freundlich constant, respectively. When the $1/n$ value is between 0 and 1, it indicates a favorable adsorption process.

In this study, Langmuir and Freundlich isotherms for the removal of Cr (VI) are shown in Fig. 5. Moreover, parameters obtained from the adsorption isotherms are given in Table 2. It was observed that the Langmuir isotherm model provides a better fit for experimental data when compared to correlation coefficients (R^2). It was an indication of the monolayer adsorption of Cr (VI) ions on the biochar surface. q_m and b values were determined as 9.0009 mg/g and 0.0792 L/mg, respectively. In addition, the R_L value was calculated as 0.3870 which signified a favorable adsorption process. When examined maximum adsorption capacity of biochars synthesized from functionalized carbonous material (2.5 mg/g), municipal sludge (7.0 mg/g), pineapple peel (7.4 mg/g), rice straw crop residue (11.6 mg/g) for removal of Cr (VI), biochar synthesized by co-pyrolysis of olive pomace and crude oil showed promising adsorption capacity as a new adsorbent in this study [60].

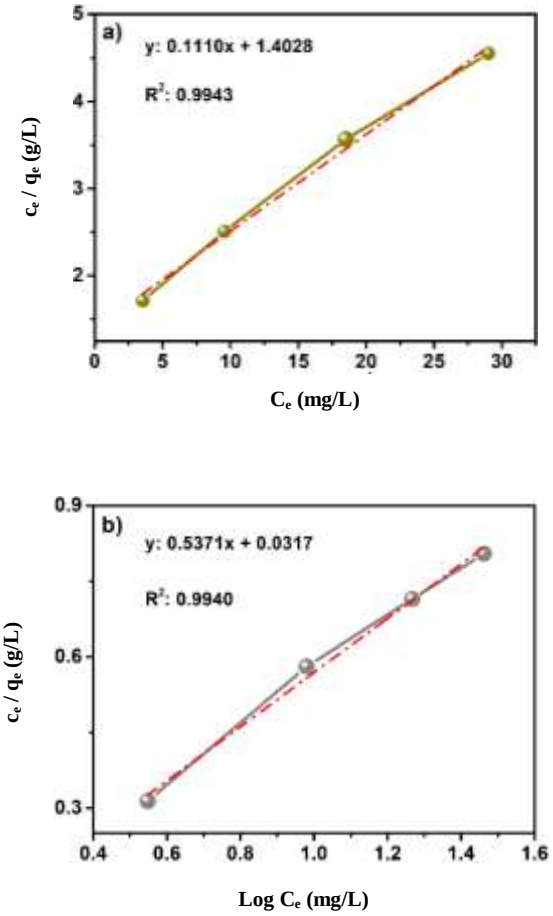

Fig. 5: a) Langmuir and b) Freundlich isotherms of Cr (VI) adsorption at optimum experimental conditions.

Adsorption Kinetics

Adsorption kinetic models are utilized to examine the controlling mechanism of adsorption processes such as diffusion control or mass transport and chemical reaction processes [61]. In this study, pseudo-first-order and pseudo-second-order kinetic models were applied to the experimental data. The pseudo-first-order and pseudo-second-order kinetic models are defined by the following linearized Equation (6) and Eq. (7) [62].

$$\log(q_e - q_t) = \log q_e - K_1 t \quad (6)$$

$$t/q_t = 1/K_2 q_e^2 + (1/q_e)t \quad (7)$$

Table 2: Langmuir and Freundlich isotherm parameters for removal of Cr (VI).

Langmuir parameters				Freundlich parameters		
q_m (mg/g)	b (L/mg)	R^2	R_L	K_f (mg/g)	n	R^2
9.0009	0.0792	0.9943	0.3870	1.0757	1.8619	0.9940

Table 3: Adsorption kinetic parameters for Cr (VI) removal.

Pseudo first order			Pseudo second order		
q_e (mg/g)	K_1 (min^{-1})	R^2	q_e (mg/g)	K_2 (g /(mg min))	R^2
0.3865	0.05296	0.8972	1.893	1.6464	0.9999

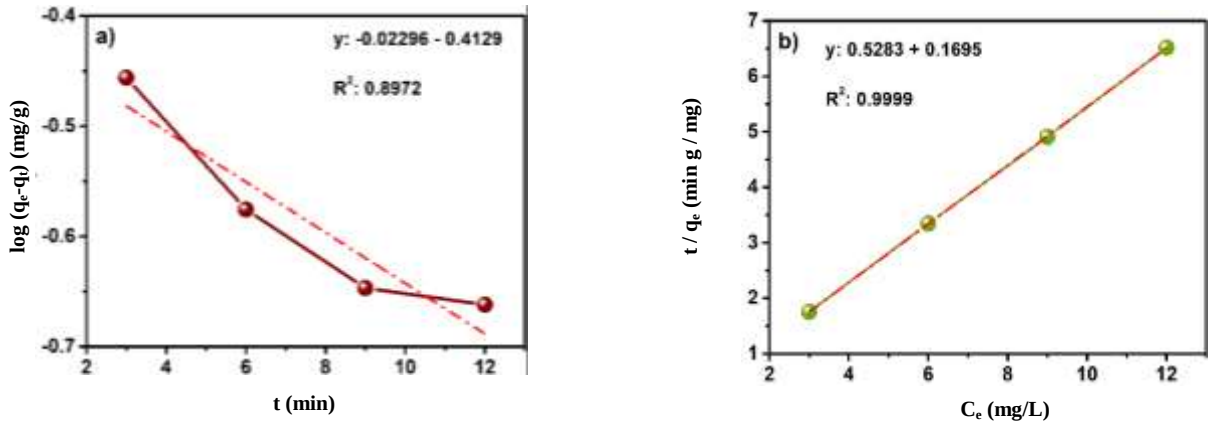

Fig. 6. a) Pseudo-first order and b) pseudo-second-order kinetic models of Cr (VI) adsorption at optimum experimental conditions.

Where q_t (mg/g) is adsorption capacity at time *t*, and q_e (mg/g) is adsorption capacity at equilibrium. K_1 (min^{-1}) is the first-order rate constant and K_2 (g/(mg min)) is the second-order rate constant.

Adsorption kinetic curves for removal of Cr (VI) are shown in Fig. 6, while parameters of the pseudo-first-order, as well as pseudo-second-order kinetic models, are given in Table 3. It was seen that the pseudo-second-order kinetic model represented a higher R^2 value (0.9999). It can be explained that chemical adsorption involving the balancing forces through the exchange or sharing of electrons between the adsorbent and the adsorbate was a possible rate-limiting step for Cr (VI) removal [63]. The results were similar to that of the adsorption processes including biochar as an adsorbent.

Adsorption Thermodynamics

To determine whether an adsorption process was spontaneous or not, thermodynamic parameters were calculated [61]. In the calculation of thermodynamic parameters such as changes in Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$), experimental data obtained at different temperatures (303, 313, and 323 K) were used. Thermodynamic parameters were obtained by the following van't Hoff Equations (8) and (9).

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

$$\ln K_d = \Delta S^{\circ}/R + \Delta H^{\circ}/RT \quad (9)$$

$$K_d = q_e/C_e \quad (10)$$

where *R* (8.314 J/(mol..K) is gas constant and *T* (K) is temperature. K_d, distribution coefficient, was calculated using Equation (10) [64]. After calculating the K_d at different temperatures, the slope and intercept point were determined by plotting ln K_d versus T^{-1} as shown in Fig. 7. And also, thermodynamic parameters for removal of Cr (VI) are given in Table 4. Negative values of ΔG°

Table 4: Thermodynamic parameters for removal of Cr (VI) removal.

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/(mol. K))
303	-18.7125	-100.7989	-0.2719
313	-14.9773		
323	-13.3168		

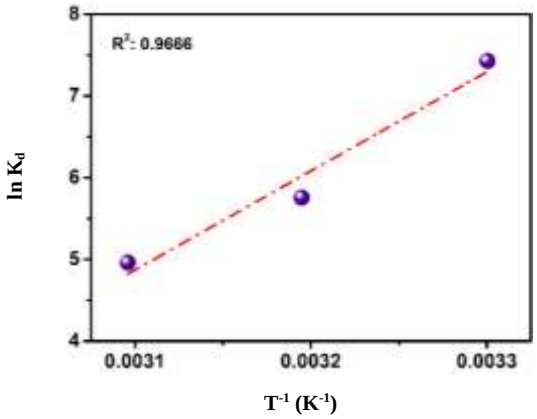

Fig. 7: ln K_d versus T^{-1} for estimation of thermodynamic parameters of Cr (VI) adsorption at optimum experimental conditions.

at different temperatures indicated that the adsorption process was carried out spontaneously. The negative ΔH° value expressed that the Cr (VI) adsorption was exothermic, while the negative ΔS° value showed a decrease in randomness at the solid-liquid interface during the adsorption. The results were in line with many studies related to Cr (VI) adsorption [41].

CONCLUSIONS

Biochar was synthesized by co-pyrolysis of olive pomace and crude oil. The low-cost and environmentally friendly biochar was evaluated as an adsorbent for Cr (VI) removal for the first time in this study. The structural, morphological properties and elemental composition of biochar were investigated using various analyses before and after Cr (VI) adsorption. The effects of adsorption parameters on the Cr (VI) adsorption were studied in detail. The optimum experimental conditions were found to be at pH: 1.5, contact time: 15 min, Cr (VI) initial concentration: 20 mg/L, biochar dose: 0.4 g, and temperature 303 K. The maximum percentage removal of Cr (VI) was specified as 82.3%, under the optimum experimental conditions. Adsorption experimental data was well-fitted to Langmuir adsorption isotherm with the maximum adsorption capacity of 9 mg/g. The adsorption process of Cr (VI) was adequately described by the pseudo-second-order kinetic model. The thermodynamic parameters indicated that the adsorption of Cr (VI) was an exothermic process and spontaneous. The results showed that the novel biochar can be a potential low-cost and effective adsorbent in adsorption processes. In addition, the synthesis of biochar from olive pomace contributed to decreasing environmental pollution preventing waste accumulation. In light of the results, in future work, the reusability of the biochar can be examined for Cr (VI) removal depending on eluent type and concentration, contact time, and temperature. And also, the biochar can be evaluated as a potential adsorbent for different heavy metals and dyes.

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