Biochar-SO prepared from pea peels by dehydration with sulfuric acid improves the adsorption of Cr^{6+} from water

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Abstract

A new biochar was produced from pea peel residues by the dehydration process. The effect of the obtained new biochar on the ability to remove Cr^{6+} ions from the aqueous solution was investigated. Biochar-SO was obtained from pea peel by dehydration of biochar with 50% sulfuric acid. The obtained biochars were characterized by Fourier transform infrared (FT-IR); Brunauer, Emmett and Teller (BET); Barrett-Joyner-Halenda (BJH); thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); scanning electron microscope (SEM); and energy-dispersive X-ray (EDAX) analyses. The optimum pH value for Cr^{6+} ion removal was determined as 1.48. The maximum removal percentage of Cr^{6+} ions was 90.74% for Biochar-SO of $100 \text{ mg} \cdot \text{L}^{-1}$ Cr^{6+} ions initial concentration and $1.0 \text{ g} \cdot \text{L}^{-1}$ adsorbent dosage. The maximum adsorption capacity (Q_m) of biochar-SO was $158.73 \text{ mg} \cdot \text{g}^{-1}$. The data obtained were analyzed with Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models. In addition, the data obtained from these isotherm models were tested using different error functions (hybrid error function (HYBRID), average percent errors (APE), the sum of the absolute errors (EABS), chi-square error (X^2), and Marquardt's percent standard deviation (MPSD and the root mean square errors (RMS)) equations. It was the Freundlich isotherm model that best fits the experimental data of biochar-SO. Kinetic data were evaluated by pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich, and intraparticle diffusion models. The adsorption rate was primarily controlled by the PSO rate model with a good correlation ($R^2 = 1$). The adsorption mechanism of biochar-SO to remove Cr^{6+} ions can be based on electrostatic interaction and ion exchange with exchangeable cations in biochar such as aluminum, silicon, and calcium ions for chromium. The results indicate that biochar-SO is a promising adsorbent for the adsorption of Cr^{6+} ions that can be employed repeatedly without substantial loss of adsorption effectiveness.

Keywords Biochar · Pea peels · Chromium(VI) · Adsorption · Dehydration

1 Introduction

Water is the most basic substance necessary for the life of all living things. Therefore, the call of countries to protect their water resources is increasing day by day [1–3]. Organic pollution and heavy metal pollution, which are the main pollutions of water, are constantly increasing with the development of modern agriculture and industry [4–7]. Metallurgy, electroplate, natural minerals and equipment, etc. are the main cause of heavy metal pollution [1, 8, 9]. Chromium (Cr) is an element in the heavy metal group and is widely used in textile industries, electroplating, steel production, pigment and dye synthesis, leather tanning, wood protection, etc. industries [10–12]. Therefore, since the wastes from such industries contain high levels of Cr ions, their direct discharge to soil or water causes serious environmental problems. Chromium ions are usually found

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in aqueous media in either a relatively harmless trivalent form or, even in low concentration, a toxic, carcinogenic, and mutagenic hexavalent state [11, 13–15]. For this reason, heavy metal-containing wastewater and sewage treatment are of great importance. Scientists have proposed different methods such as membrane separation, chemical precipitation, adsorption, biological treatment, redox, and ion exchange to remove heavy metal ions from wastewaters [16–23]. Among these techniques, the adsorption technique has been the preferred method since it eliminates some disadvantages such as high equipment cost, toxic sludge, and other waste production seen in other methods [24–29]. Zeolite, activated carbon, chitosan, graphene, and agroforestry wastes are widely used in the treatment of Cr^{6+} ions, a toxic heavy metal, from wastewater [30–38]. Activated carbon (AC) is one of the most famous and most efficacious adsorbents known in the world, but its expensiveness limits its widespread use [39–41]. For this reason, biochar, which is offered as an alternative to AC, is also widely used in the adsorption process [26–28]. Comparing studies using biochar [42, 43] and activated carbon [44–46], both reported higher removal efficiency with less cost and modification. In environments where agriculture and forestry production is limited, activated carbon and biochar are obtained from the pyrolysis of waste biomass residues. Compared to activated carbon, biochar is produced at relatively lower temperatures and has more functional groups on its surface, although it has a lower surface area and less porosity after the activation process [47, 48]. Since biochars have a non-carbonized fraction with carboxyl, hydroxyl, and phenolic surface functional groups on their surfaces, they are easier to bind effectively to water pollutants compared to activated carbons [49]. Adsorption capacities of biochars can be increased by using modification methods such as mineral impregnation, biochar surface reduction, nanoscale formation, or oxidation [26–28, 46]. The activation process is essential for the biochar, which will be obtained from raw material with relatively low porosity, to have a highly porous structure and to increase its adsorption capacity. This process is carried out into two ways, chemical and physical activation. While chemical activation takes place by reacting chemicals such as ZnCl_2 , KOH , H_2SO_4 , HNO_3 , and H_3PO_4 with the raw material in an inert environment at high temperature, no chemicals are used in physical activation, and it is the process of carbonization under an atmosphere of high-temperature carbon dioxide (CO_2) or water vapor. Most studies report that adsorbents obtained by chemical activation are more effective than adsorbents obtained by physical activation [50–55]. For the removal of chromium ions, scientists have worked with the following adsorbents in the last two decades: tea factory waste [56], moss (*Hylocomium splendens*) [57], rice straw [58–60], pomegranate

husk [61, 62], lichen (*Parmelina tiliaceae*) [63], red algae (*Pterocladia capillacea*) [64, 65], chemically modified seaweed (*Cystoseira indica*) [66], sawdust, wool, almond shells, olive cake, charcoal, pine needles, and cactus leaves [67].

In this study, pea peels based biochar is used due to their easy preparation, surface functional groups, easy supply, and efficient treatment. Research on adsorption applications with pea peels based biochar for Cr^{6+} ion removal is limited. Biochar-SO produced from pea *Pisum sativum* peels, which is a low-cost agricultural waste material, by dehydration using H_2SO_4 was tested for its efficiency in Cr^{6+} ion removal from wastewaters. The effects of pH, initial adsorbent concentration, biochar-SO dose, and contact time between biochar-SO and Cr^{6+} ions as the removal conditions of Cr^{6+} ions from aqueous solution were investigated. Adsorption isotherms of chromium ions on Cr^{6+} ion as adsorbent were also investigated to determine the structure of adsorption and its maximum adsorption capacity.

2 Materials and methods

2.1 Materials

Pea peel (*Pisum sativum*) obtained from a local market was used for the production of biochar-SO. Sulfuric acid (H_2SO_4 , M.W. = 98.07 g, assay (acid-metric) 99%) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, M.W. = 294.19 g, assay (99%)) were supplied from Sigma-Aldrich. Potassium dichromate standard stock solution was prepared from potassium dichromate. BDHZ chemicals LTD Poole-England provided 1,5-diphenylcarbazide as a reagent for Cr^{6+} ions. In the experiments, a digital spectrophotometer (Analytic Jena (SPEKOL1300 UV/Visible spectrophotometer)) with matching glass cells with a 1-cm optical path, a shaker (JSOS-500), and a pH meter JENCO (6173) were used.

2.2 Preparation of biochar-SO

Pea peels were properly washed many times with faucet water to eliminate dust and then dried for 48 h at 105 °C. The dried pea peels were ground and crushed. The crushed pea peels (200 g) were cooked for 2 h in a 1.0 L solution of 50% H_2SO_4 in a refluxed system, then filtered, and washed with pure water until the filtrate became neutral, followed by washing with ethanol. The finished output of biochar was dried overnight at 105 °C and then weighed. Carbonization and sulfonation processes happened with this way of preparation [26–28]. The biochar produced in this process was designated biochar-SO.

2.3 Batch adsorption experimental

A stock solution of Cr^{6+} ions (1000 mg L^{-1}) was obtained by dissolving 2.8289 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1 L of pure water, and this solution was diluted to the desired concentrations for the calibration standard curve and adsorption tests. The adsorption capabilities, thermodynamic, and kinetic characteristics of biochar-SO were determined using batch adsorption studies. A series of Erlenmeyer flasks (300 mL) was shaken at 200 rpm (selected depending on our previous study) for a specified duration with 100 mL of various concentrations of Cr^{6+} ion solution and varying volumes of biochar-SO. With 0.1-M HCl or 0.1-M NaOH , the pH of the sample was changed to the appropriate levels. Concentration measurement of Cr^{6+} ions was performed by taking 0.1 mL sample from the solution in the Erlenmeyer flask and separating from the adsorbent, at various intervals and equilibrium. The concentration of Cr^{6+} ions was measured using spectrophotometry and the chromogenic agent 1,5-diphenylcarbazine ($\lambda_{\text{max}} = 540 \text{ nm}$) [68, 69]. The equilibrium adsorption capacities (q_e) were estimated using Eq. (1):

$$q_t = \frac{(C_0 - C_t)}{W} \times V \quad (1)$$

where the adsorption capacity (q_t) ($\text{mg adsorbate/g adsorbent}$) is the adsorbent's ability to remove Cr^{6+} ions from a solution at a certain time. C_0 (mg/L) is the initial concentration of Cr^{6+} ions; C_t (mg/L) is the residual concentration of the Cr^{6+} ions after the adsorption process had been completed for a given time. The following equation can be used to calculate the elimination % of Cr^{6+} ions from an aqueous solution (2).

$$\text{Removal}(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

The influence of pH on Cr^{6+} ion adsorption was examined by mixing 0.1 g of the adsorbent with 100 mL of Cr^{6+} ion solution of a concentration of 100 mg/L for biochar-SO (0.1 g) with initial pH values varying between 1.48 and 9.41 . A total of 0.1-M HCl and 0.1-M NaOH solutions were used to modify the pH levels. At 25°C , the suspensions were agitated at 200 rpm for 180 min before being sampled for Cr^{6+} ion measurement.

For the isotherm investigation, 100 mL of Cr^{6+} ion solutions were mixed at 200 rpm for 3 h at 25°C with varying initial concentrations of Cr^{6+} ion solutions ($50\text{--}300 \text{ mg/L}$) and various amounts of biochar-SO (0.2 to 0.6 g).

At 25°C , the effect of adsorbent dosage and contact time on Cr^{6+} ion removal was investigated by shaking 100 mL of initial Cr^{6+} ion concentration for biochar-SO

with varied adsorbent dosages of ($0.2, 0.3, 0.4, 0.5$, and 0.6 g) at different interval times at 25°C .

2.4 Biochar-SO characterization

The adsorption–desorption isotherm of N_2 on biochar-SO was calculated at the boiling point of nitrogen gas. The surface area and pore analyzer (BELSORP – Mini II, BEL Japan, Inc.) was used to assess the BET surface area (S_{BET}) of the biochar using nitrogen adsorption at 77 K [70, 71]. The BET plot was used to calculate surface area (S_{BET}) (m^2/g), monolayer volume (V_m) ($\text{cm}^3 (\text{STP}) \text{ g}^{-1}$), total pore volume (p/p_0) (cm^3/g), mean pore diameter (nm), and energy constant (C) for the isotherm. The following equation was used to compute the average pore radius (3).

$$r(\text{nm}) = \frac{2V_T(\text{mLg}^{-1})}{a_{s,\text{BET}}(\text{m}^2\text{g}^{-1})} \times 1000 \quad (3)$$

To determine the mesopore surface area (S_{mes}), micropore surface area (S_{mi}), mesopore volume (V_{mes}), and micropore volume (V_{mi}) of biochar-SO, Barrett-Joyner-Halenda (BJH) method was used by using BELSORP analysis program software.

The BJH method [72] is used to compute the pore size distribution from the desorption isotherm.

The surface morphology of the biochar-SO sample was investigated using a scanning electron microscope (SEM) (QUANTA 250) in conjunction with an energy dispersive X-ray spectrometer (EDX) for elemental analysis.

The functional groups on the biochar-SO surface were investigated using Fourier transform infrared (FT-IR) spectroscopy (VERTEX70) and ATR unit model V-100.

Thermal analyses were carried out using the SDT650-simultaneous thermal analyzer device at a temperature range of 25°C to 1000°C , at a temperature increase rate of $5^\circ\text{C}/\text{min}$.

2.5 Theoretical background

It is assumed in the Langmuir model [73] that adsorption takes place in monolayers on a surface and that there is no transmigration of adsorbate along the plane of the surface [74]. In the Langmuir linear equation, q_e (mg/g) represents the equilibrium adsorption capacities; C_e (mg/L) represents the equilibrium concentration; Q_m (mg/g) represents the maximum adsorption capacity of a monolayer; and K_a (L/mg) represents a constant that represents the adsorption equilibrium sorption energy; the equation can be written as Eq. (2) [60, 75, 76].

Figure 1 shows the Freundlich model [77] in its linear version, as indicated in Eq. (4). In this equation, K_F and $1/n$ express the relative adsorption capacity constant and the

Fig. 1 FT-IR analysis of the raw pea peels and biochar-SO

intensity of the adsorption or the degree of surface heterogeneity, respectively. When the value of $1/n$ approaches zero, it becomes more heterogeneous. The linear version of the Temkin isotherm equation is given by Eq. (5) [60, 78–82], which is the linear form of the equation. It is calculated with $B_T = (RT)/b$ in this equation, b is proportional to the heat of adsorption, with the equilibrium binding constant A_T (L/mg) equal to the maximum binding energy, with the absolute temperature T (K), and the universal gas constant R (8.314 J/mol K) [83, 84].

A model developed by Dubinin and Radushkevich [85–87] is used to evaluate the apparent free energy of porosity and the characteristic of adsorption. The Dubinin-Radushkevich isotherm does not make any assumptions about the surface homogeneity or the continuous sorption potential. The Dubinin-Radushkevich (D-R) model has been widely used to solve the linear Eqs. (6) and (7), which are shown in Table 1.

Pseudo-first-order (PFO) adsorption is represented by the linear Eq. (8) [88], where q_t (mg/g) is the adsorption

capacity at time t (min); and k_1 (L/min) is the rate constant of PFO adsorption. It should be possible to estimate the slope and intercept of the plot by plotting $\log(q_e - q_t)$ with time. This should result in a linear relationship from which the value of k_1 and the projected value of q_e can be calculated. Using Eq. (9), Ho et al. [89] derive the linear PSO model, in which k_2 ($\text{g mg}^{-1} \cdot \text{min}^{-1}$) is the adsorption second-order rate constant, which is utilized to compute the initial sorption rate, h , $h = k_2 q_e^2$.

The intercept and slope of the plots of t/q_t vs. t , as well as the values of k_2 and q_e , may be evaluated from the values of k_2 and q_e , respectively. As a general rule, the linear Elovich kinetic model is represented by Eq. (10), in which α (mg/g min) and β (g/mg) are the initial adsorption rate and desorption constant, respectively. It should be possible to plot the data to see that q_t is related to $\ln(t)$ in a linear fashion with slope $(1/\beta)$ and intercept $(1/\beta) \ln(\alpha\beta)$ [90–92]. With the help of Eq. (11) [93, 94], we may investigate the potential of intraparticle diffusion. As the value of the intercept C grows, the barrier to external mass transfer increases proportionally. When plotting q_t against $t^{1/2}$, the intraparticle diffusion rate constant ($\text{mg g}^{-1} \cdot \text{min}^{-1/2}$) can be calculated directly from the slope of the regression line of the regression line of the plot of q_t versus $t^{1/2}$ (Table 2).

Using Eq. (12), which displays the fit between experimental and anticipated data acquired from isotherm model curves [95], the average percentage error (APE) can be calculated (Table 3). Equation (13) [96, 97] expresses the fractional error function for hybrid fractional error. It is given as Eq. (14) the chi-square error, X^2 , as determined by Ho et al. [97]. Marquart's percentage standard deviation (MPSD) [60,

Table 1 The isotherm models used in other studies of Cr^{6+} ion adsorption by biochar-SO [60]

Model name	Equation	Equation
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} C_e$	(3)
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	(4)
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$	(5)
Dubinin-Radushkevich	$\ln q_e = \ln Q_m - K \epsilon^2$	(6)
	$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$	(7)

Table 2 The kinetic models used in the kinetic study of Cr^{6+} ion adsorption by biochar-SO [60]

Model name	Equation	Equation
Pseudo-first-order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$ (8)	
Pseudo-second-order	$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$ (9)	
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t)$ (10)	
Intraparticle diffusion	$q_t = K_{dif}t^{1/2} + C$ (11)	

95] can be evaluated using Eq. (15). Equation (16) calculates the absolute error sum (EABS) between points [60, 95]. According to Eq. (17), the root means square errors (RMSE) can be calculated [60, 95].

3 Results and discussion

3.1 The characteristics of biochar-SO

The FT-IR method was used to detect the functional groups in the biochar-SO sample that had been manufactured [26–28]. Figure 1 illustrates the FT-IR spectra of raw pea peel and biochar-SO, as well as the spectrum of the biochar-SO. Specifically, the strong band at $3224\text{--}3378\text{ cm}^{-1}$ indicates the O–H stretching oscillation, and it was found in both raw pea peel and biochar-SO. The band at $2919\text{--}2929\text{ cm}^{-1}$ is attributed to the –CH stretching oscillation and was found in raw pea peel and biochar-SO, among other things. The adsorption peak at 1701 cm^{-1} can be attributed to C=O stretching of the carboxyl group, which was present in biochar-SO but was not present in the raw pea peel, demonstrating the synthesis of a new carboxylic group in biochar-SO (Fig. 1). The band at 1620 cm^{-1} indicates the presence of the C=O stretching oscillation, which was nearly completely absent in the raw pea peel

Table 3 The errors analysis models used in the isotherm study of Cr^{6+} ion adsorption by biochar-SO [60]

Model name	Equation	Equation
APE	$APE(\%) = \frac{100}{N} \sum_{i=1}^N \left \frac{q_{e, \text{isotherm}} - q_{e, \text{calc}}}{q_{e, \text{isotherm}}} \right _i$	(12)
HYBRID	$HYBRID = \frac{100}{N-P} \sum_{i=1}^N \left \frac{q_{e, \text{isotherm}} - q_{e, \text{calc}}}{q_{e, \text{isotherm}}} \right _i$	(13)
Chi-square	$X^2 = \sum_{i=1}^N \frac{(q_{e, \text{isotherm}} - q_{e, \text{calc}})^2}{q_{e, \text{isotherm}}}$	(14)
MPSD	$MPSD = 100 \sqrt{\frac{1}{N-P} \sum_{i=1}^N \left(\frac{q_{e, \text{calc}} - q_{e, \text{isotherm}}}{q_{e, \text{isotherm}}} \right)^2}$	(15)
EABS	$EABS = \sum_{i=1}^N q_{e, \text{calc}} - q_{e, \text{isotherm}} _i$	(16)
RMS	$RMS = 100 \sqrt{\frac{1}{N} \sum_{i=1}^N \left(1 - \frac{q_{e, \text{calc}}}{q_{e, \text{isotherm}}} \right)^2}$	(17)

and biochar-SO. Because the C–O functional group was weak, the peak at $1414\text{--}1436\text{ cm}^{-1}$ indicates that the raw pea peel and biochar-SO both included the C–O functional group. Pea peel contains oxygenated carbon chains, with the presence of oxygenated carbon chains peaking at 1239, 1064, and 1002 cm^{-1} . This reflects the C–O–C asymmetric stretching functional group for the raw pea peel. The dehydration with H_2SO_4 led to the formation of new peaks that appeared at 1151.5, 1037, 879, and 576.6 cm^{-1} , which are due to the formation of sulfonic acid and sulfoxide groups in biochar-SO. These new peaks prove the formation of the biochar-SO due to the treatment of pea peels with 50% H_2SO_4 .

The BET and BJH methods were used to evaluate the textural parameters of the biochar-SO. The BET-specific surface area, mesopore area, total pore volume, mesopore volume, monolayer volume, mean pore diameter, and mesopore distribution peak for the biochar-SO is shown in Fig. 2 [26–28]. Figure 2 shows that the BET-specific surface area of biochar-SO was $19.132\text{ m}^2/\text{g}$ and the monolayer volume value of biochar-SO was $4.94\text{ cm}^3/\text{g}$. The total volume value of biochar-SO was $0.022\text{ cm}^3/\text{g}$ and the mean pore diameters of biochar-SO was 4.45 nm (mesopores). The meso surface area of biochar-SO was $15.94\text{ m}^2/\text{g}$ and the mesopore distribution peak values of biochar-SO was 1.66 nm .

Raw pea peel and biochar-SO micrographs were analyzed by a scanning electron microscope (Fig. 3). The porous structure of prepared biochar with varied sizes, as shown in Fig. 3b of biochar-SO, indicates that the surface area is rather high.

Chemical compositions of the biochar-SO sample were analyzed with EDX (Table 1). Table 4 shows the absence of nitrogen and the presence of 34.24% oxygen and 11.68% of sulfur besides 50.57% of carbon.

The thermogravimetric profile of the raw materials pea peels and biochar-SO samples as a function of temperature is shown in Fig. 4a [26–28]. In accordance with Fig. 4a, the degradation of the raw material pea peels and a biochar-SO sample takes place in three stages. When the sample is heated to temperatures varying from 50 to $150\text{ }^\circ\text{C}$, the first step results in the loss of surface-bound water and moisture present in the sample, with weight losses of approximately 4.04 and 8.78% for the raw material pea peels and biochar-SO sample, respectively, in the first step. The second weight loss phase resulted in approximately 63.68% weight loss at $150\text{--}350\text{ }^\circ\text{C}$ and 20.53% weight loss at $150\text{--}275\text{ }^\circ\text{C}$ for the raw material pea peels and biochar-SO sample, respectively, in the second weight loss step. The third weight loss phase resulted in approximately 5.014% weight loss at $350\text{--}1000\text{ }^\circ\text{C}$ and 25.70% weight loss at $275\text{--}1000\text{ }^\circ\text{C}$ for the raw materials pea peels and biochar-SO sample, respectively, in the third weight loss step. The weight stayed in the same order as the raw material pea peels and biochar-SO, and the

Fig. 2 a Plot of the adsorption–desorption, b plot of the BET analysis, and c plot of the BJH analysis of biochar-SO.

Fig. 3 SEM image of a the raw pea peels, b biochar-SO

Table 4 EDX analysis data of biochar-SO sample

Elements	Wt%	At%
C	50.57	60.44
O	34.24	30.73
N	ND	ND
S	11.68	5.23

ND not detected.

percentages of 27.27 and 45.10% were achieved, indicating that biochar-SO is more stable than the raw materials.

Differential thermal analysis (DTA) can only be utilized as a fingerprint for identifying purposes; however, the majority of the time, this method is employed for phase diagram determination, heat change measurements, and decomposition in diverse environments (Fig. 4b). Comparing the DTA curves of raw pea peel and biochar-SO samples, the raw pea peel sample showed two peaks at flow T_f temperature (76.67 and 342.45 °C), while biochar-SO sample showed two peaks at a lower flow T_f temperature (75.95 and 213.84 °C). According to this analysis result, the pea peel sample shows more stability than biochar-SO. However, the pyrolysis of both the raw pea-peel and biochar-SO samples reveals two distinct degradation peaks that can be distinguished from one another. After being treated with sulfuric acid, the degradation peaks are reduced to two peaks. Following acid treatment and dehydration, these findings suggest that the degree of degradation of the pea peel has been lowered.

It is possible to compare materials by using differential scanning calorimetry, which measures thermal transitions. Figure 5 depicted the DSC of the raw pea peel and

biochar-SO in comparison to each other. Crystallization temperature (T_C) values for all samples were below 100 °C, indicating that the crystallization of water molecules was responsible for their formation. It was determined by DSC that the T_C of the pea peel raw material was between 348.29 and 758.59 °C. The DSC analysis of biochar-SO revealed a crystallization temperature (T_C) of 219.84 degrees Celsius [26, 27].

3.2 Adsorption of Cr^{6+} ions on biochar-SO

3.2.1 Effect of initial pH

Solution pH is among the most significant parameters affecting adsorption. The solution pH affects the amino, carboxyl, and hydroxyl groups on the biochar surface and creates a repulsive/attractive force between the adsorbent and the adsorbate. By using 1 g·L⁻¹ of biochar-SO, the amount of Cr^{6+} ions adsorbed at equilibrium (q_e) and the percentage of effacement of these ions were determined in the experimental studies carried out in a solution containing 100 mg·L⁻¹ of Cr^{6+} ions and at room temperature (25 ± 2 °C). Figure 6 shows how the adsorption of Cr^{6+} ions changes with pH over 24 h after contact time in the pH range of 1.48 to 9.41. For the removal of Cr^{6+} ions using biochar-SO, it is seen in Fig. 6a that the highest Cr^{6+} ion removal (90.74%) occurred at pH 1.48. Figure 6b shows the amount of Cr^{6+} ions at equilibrium (q_e , mg·g⁻¹) attached to the biochar-SO surface in the pH range of 1.48 to 9.41. According to Fig. 6b, when the adsorption of Cr^{6+} ions to biochar-SO is examined, the amount of Cr^{6+} ions adsorbed at equilibrium (q_e)

Fig. 4 a TGA plot of the raw pea peels and biochar-SO, b DTA plot of the raw pea peel and biochar-SO

Fig. 5 DSC plot of the raw pea peel and biochar-SO

slightly decreased (from 90.74 to 82.63 $\text{mg}\cdot\text{g}^{-1}$) with the increase in pH value from 1.48 to 3.52, and then we see that it remains constant up to 9.41 pH (81.80 $\text{mg}\cdot\text{g}^{-1}$). Therefore, it was concluded that the optimum working pH value for the removal of Cr^{6+} ions on biochar-SO is 1.48. The percentages of Cr^{6+} ion removal obtained at all pH values studied ranged between 81.80 and 90.74%. There are two

proposed mechanisms in the adsorption process of Cr^{6+} ions on biochar-SO: (1) There is an attraction between the positively charged biochar-SO and the negatively charged Cr^{6+} ions and (2) Cr^{6+} ions are reduced to Cr^{3+} ions and form complexes with carboxyl and hydroxyl groups on biochar-SO. Between pH 1 and 4, electrostatic attraction forces occur between HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$, which are the dominant types

(a)

(b)

Fig. 6 Sorption of Cr^{6+} ions onto biochar-SO as a function of **a** pH on the removal %; **b** on the q_e ($\text{mg}\cdot\text{g}^{-1}$) of Cr^{6+} ions ($\text{Cr}^{6+} = 100 \text{ mg}\cdot\text{L}^{-1}$, adsorbent = $1.0 \text{ g}\cdot\text{L}^{-1}$, temperature = 25°C)

of Cr^{6+} ions, and biochar-SO proving that biochar-SO is an effective adsorbent in adsorbing Cr^{6+} ions.

3.2.2 Effect of contact time

The effect of contact time on Cr^{6+} ions, which is different beginning concentrations ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$), adsorption by biochar-SO was examined and the results are illustrated in Fig. 7. The removal rate of the Cr^{6+} ions of the biochar-SO had reached 86–97% in the initial 15–30 min (Fig. 7). The reason for this high removal in the first 30 min can be shown that there is sufficient active adsorption site on biochar-SO at the initial stage of adsorption. As these regions are filled with Cr^{6+} ions in time, there is not enough active site left, so the removal % has followed a stable course. After 60 min, the adsorption of Cr^{6+} ions is nearly invariable. At the end of 3 h, it was observed that there were no significant changes in Cr^{6+} ion concentrations, and the values were measured as 99% for all biochar-SO doses. If all the initial Cr^{6+} ion concentrations studied are compared, although they show similar removal %, the reason why the beginning concentration of $50\text{ mg}\cdot\text{g}^{-1}$ is slightly more than the initial concentration of $300\text{ mg}\cdot\text{g}^{-1}$ removal % is the limited number of active substances on biochar-SO. This is because the regions hold as many ions as they can and the excess ions remain in the solution.

3.2.3 Effect of initial Cr^{6+} ion concentration

Another significant parameter in the adsorption process is the initial concentration of the adsorbed substance. Figure 8 shows the effect of solutions with different initial Cr^{6+} ion

Fig. 7 The effect of contact time on the adsorption of Cr^{6+} ions of biochar-SO (initial concentration of Cr^{6+} ions: $50\text{--}300\text{ mg}\cdot\text{L}^{-1}$, adsorbent dosage = $6.0\text{ g}\cdot\text{L}^{-1}$, temperature = $25\text{ }^{\circ}\text{C}$)

Fig. 8 The effect of Cr^{6+} ions initial concentration ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$) and using biochar-SO doses ($2\text{--}6\text{ g}\cdot\text{L}^{-1}$) on q_e ($\text{mg}\cdot\text{g}^{-1}$) (temperature = $25\text{ }^{\circ}\text{C}$)

concentrations on the adsorption capacity at equilibrium (q_e). To find the effect of biochar-SO dosage on adsorption capacity at equilibrium (q_e), the adsorbent concentration ($2.0\text{--}6.0\text{ g}\cdot\text{L}^{-1}$) and the beginning Cr^{6+} ion concentration ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$) was studied at $25\text{ }^{\circ}\text{C}$ at a pH of 1.48. It can be seen in Fig. 8 that the amount of Cr^{6+} ions adsorbed at equilibrium (q_e) decreases regularly as the biochar-SO dosage increases from 2.0 to $6.0\text{ g}\cdot\text{L}^{-1}$ at the same initial Cr^{6+} ion concentration. If the equilibrium (q_e) adsorption capacities are examined in the elimination of chromium ions by using biochar-SO adsorbent at different doses ($2.0\text{--}6.0\text{ g}\cdot\text{L}^{-1}$) for beginning Cr^{6+} ion concentrations ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$), these values range from 24.69 to 135.32, 16.56 to 91.42, 12.44 to 70.52, 9.97 to 56.69, and 8.31 to 49.53 $\text{mg}\cdot\text{g}^{-1}$ for biochar-SO dosages ($2.0, 3.0, 4.0, 5.0,$ and $6.0\text{ g}\cdot\text{L}^{-1}$), respectively. Therefore, it is seen in Fig. 8 that increasing the beginning Cr^{6+} ion concentration in all biochar-SO dosages leads to an increase in the amount of Cr^{6+} ions adsorbed at equilibrium (q_e).

3.2.4 Effect of adsorbent dosage on Cr^{6+} ion adsorption

The effect of adsorbent dosage on the adsorption process of Cr^{6+} ions by biochar-SO was examined by varying the adsorbent dosage ($2\text{--}6\text{ g}\cdot\text{L}^{-1}$), the beginning concentration of Cr^{6+} ions ($50\text{--}300\text{ mg}\cdot\text{L}^{-1}$), adsorption time (3 h), and solution temperature ($25 \pm 2\text{ }^{\circ}\text{C}$) at an initial pH of 1.48. As shown in Fig. 9a, with an increase in the quantity of biochar-SO adsorbent, the removal efficiency of Cr^{6+} ions by biochar-SO increased continuously. However, while this increase is negligible in $50\text{ mg}\cdot\text{L}^{-1}$ and $75\text{ mg}\cdot\text{L}^{-1}$ dosages, it reaches from 90 to

Fig. 9 The effect of biochar-SO in different dosages (2.0–6.0 g·L⁻¹) of different initial Cr⁶⁺ ion concentration (50–300 mg·L⁻¹) **a** on removal % and **b** on q_e (mg·g⁻¹) (temperature = 25 ± 2 °C)

100% in 100, 150, 200, and 300 mg·L⁻¹ dosages. Cr⁶⁺ ion removal was between 90 and 100% at all adsorbent dosages (2–6 g·L⁻¹) and all beginning Cr⁶⁺ ion concentrations (50–300 mg·L⁻¹) studied. The quantity of Cr⁶⁺ ions adsorbed at equilibrium (q_e) decreases with the increase of biochar-SO adsorbent dosage for all initial Cr⁶⁺ ion concentrations. Besides, the quantity of chromium ions adsorbed at equilibrium (q_e) decreases from 24.69 to 8.31, 36.75 to 12.47, 45.97 to 16.61, 69.87 to 24.95, 92.12 to 33.13, and 135.32 to 49.53 mg·g⁻¹ with increasing of the amount of biochar-SO adsorbent from 2.0 to 6.0 g·L⁻¹ for initial Cr⁶⁺ ion concentrations 50, 75, 100, 150, 200, and 300 mg·L⁻¹, respectively. It is seen in Fig. 9 that the lowest quantity of removal process at equilibrium (q_e) and maximum (%) of removal was carried out using 6.0 g·L⁻¹ of biochar-SO dosage.

3.3 Adsorption isotherms

The relationship curve between the adsorption process amount of the adsorbent and the equilibrium concentration of the adsorbent with the adsorption process at a certain adsorption temperature is expressed by the adsorption isotherm. In this study, the correlation between experimental data with different initial Cr⁶⁺ ion concentrations and Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherm models were investigated. To evaluate the isotherm parameters, linear method was tested. While Fig. 11 shows the graphs of four different isotherm models, the isotherm parameters obtained from these graphs are summarized in Table 5.

The linear form of the Langmuir model showed a high correlation coefficient (R^2) ≥ 0.981 when the biochar-SO dose was 4 g·L⁻¹. The maximum monolayer capacity (Q_m) of the biochar-SO adsorbent was calculated as 158.73 mg·g⁻¹ when the biochar-SO dosage was 2.0 g·L⁻¹. To calculate the

Table 5 Isotherm study data of adsorption of Cr⁶⁺ ions onto biochar-SO adsorbent (initial Cr⁶⁺ ion concentration = (50–300 mg·L⁻¹), adsorbent dosages = (2.0–6.0 g·L⁻¹), temperature = (25 °C)

Isotherm model	Parameters	Biochar-SO adsorbent doses (g·L ⁻¹)				
		0.2	0.3	0.4	0.5	0.6
Langmuir	Q_m (mg·g ⁻¹)	158.73	97.09	74.63	55.56	60.98
	K_L	0.10	0.278	0.60	0.94	1.34
	R^2	0.741	0.949	0.981	0.959	0.962
Freundlich	$1/n_F$	0.405	0.372	0.370	0.314	0.518
	Q_m (mg·g ⁻¹)	159	126	124	99	337
	K_F (mg ^{1-1/n} ·L ^{1/n} ·g ⁻¹)	28.36	25.96	25.62	23.27	30.99
	R^2	0.905	0.975	0.955	0.887	0.891
Temkin	A_T	2.723	5.936	10.479	23.342	15.722
	B_T	24.520	15.891	12.606	8.696	12.448
	R^2	0.770	0.912	0.975	0.927	0.946
D-R	Q_m (mol·kg ⁻¹)	75.33	54.80	48.99	42.36	42.67
	$K \times 10^6$ (mol·kJ ⁻¹) ²	2.0E-01	1.0E-01	9.0E-02	6.0E-02	6.0E-02
	E (kJ·mol ⁻¹)	1581.14	2236.07	2357.02	2886.75	2886.75
	R^2	0.610	0.715	0.870	0.924	0.914

values of $1/Q_m K_L$ and $1/Q_m$ from the parameters of the Langmuir model, C_e/q_e vs. C_e is plotted as illustrated in Fig. 10a, and the intercept and slope of this graph give these values, respectively. As seen in Table 5, the equilibrium adsorption coefficient K_L value varies between 0.1 and 1.34 in different adsorbent dosages and the R^2 value is as high as 0.981 in biochar-SO with 4 g·L⁻¹ dosage, which is evidence that Cr⁶⁺ ions hold on biochar-SO. The high R^2 coefficient in the Langmuir isotherm model indicates that Cr⁶⁺ ions are adsorbed in a single layer on the biochar-SO surface.

The Freundlich isotherm model, which correctly establishes the adsorption process as a heterogeneous phenomenon, was also used to determine the effectiveness of biochar-SO adsorbent in the removal of Cr⁶⁺ ions. To calculate the values of $\log K_F$ and $1/n_F$ from the parameters of the

Freundlich model, $\log(q_e)$ vs. $\log(C_e)$ is plotted as illustrated in Fig. 10b, and the intercept and slope of this graph give these values, respectively. The coefficient K_F , which symbolizes the relative adsorption capacity of the biochar-SO, decreased with improving adsorbent dosage (from 2.0 to 5.0 g·L⁻¹). K_F value increases when the dosage is improved from 5.0 to 6.0 g·L⁻¹. Generally, the improvement in the adsorption capacity of the adsorbent is directly proportional to the increase in the K_F value. The immensity of the Freundlich isotherm exponent $1/n$ is an index of the degree of the favorability of an adsorption process. In Table 5, since all $1/n$ values are less than 1, all the n values are above 1, varying between 1.93 and 3.18, an indicator that adsorption of Cr⁶⁺ ions on biochar-SO was favorable. The fact that the adsorption process of Cr⁶⁺ ions on biochar-SO is a suitable

Fig. 10 a Linearized Langmuir, b Freundlich, c Temkin, d D-R. e Comparison between the measured and modeled isotherm profiles for Cr⁶⁺ ions of initial concentration (50–300 mg·L⁻¹) on biochar-SO dosages (2.0–6.0 g·L⁻¹) at 25 °C.

Table 6 A few error function values of the isotherm models best suited to the experimental equilibrium data in the adsorption of Cr^{6+} ions on biochar-SO

Isotherm model	APE (%)	X^2	Hybrid	MPSD	EABS	RMS
Linear Langmuir	21.54	64.44	23.07	27.49	213.47	26.56
Freundlich	12.62	26.88	13.52	17.10	137.07	16.52
Temkin	15.02	47.68	16.09	21.17	174.55	20.45
Dubinin-Radushkevich	105.59	999.62	113.14	154.76	703.91	149.51

physical process depends on the value of n_F greater than 1. Table 5 shows that the Freundlich Q_m value for biochar-SO is $159 \text{ mg} \cdot \text{g}^{-1}$ at $2 \text{ g} \cdot \text{L}^{-1}$ adsorbent dosage. A high Q_m value indicates that Cr^{6+} ions are adsorbed so well on the biochar-SO surface. Freundlich isotherm correlation coefficient also showed a high value ($R^2=0.975$) similar to that of Langmuir isotherm.

The Temkin isotherm model, which takes into account the interaction between adsorbate and adsorbent, determines a factor for this. The Temkin model assumes that with the accumulation of adsorbed molecules or ions on the adsorbent surface, the heat of adsorption of all molecules in the layer will decrease over time. This assumption is made due to these interactions and neglecting very low and very high concentration values. The lowest and highest values obtained at five different adsorbent dosages ($2.0\text{--}6.0 \text{ g} \cdot \text{L}^{-1}$) from the Temkin isotherm were $A_T=2.72\text{--}23.34 \text{ L} \cdot \text{g}^{-1}$ and $B_T=8.69\text{--}24.52 \text{ kJ} \cdot \text{mol}^{-1}$, indicating that the adsorption of Cr^{6+} ions onto biochar-SO occurred via ion exchange, except for the $6.0 \text{ g} \cdot \text{L}^{-1}$. The value for the bonding energy was

between 8 and $16 \text{ kJ} \cdot \text{mol}^{-1}$ and thus the process implied is ion exchange. Considering the correlation coefficients of the Temkin isotherm model, it was observed that it was in the range of $0.912\text{--}0.975$ in all samples, except for the $2.0 \text{ g} \cdot \text{L}^{-1}$ adsorbent ($R^2=0.770$) dosed sample, and it can be said to agree with the experimental data.

Equilibrium data were performed to the D-R isotherm model to understand whether the adsorption of Cr^{6+} ions to Biochar-SO is physical or chemical, and the results are illustrated in Table 5. The D-R isotherm model is attributed to the Polanyi potential theory, which is applied where the adsorption process continues until the pores are filled. The apparent energy (E) value is used to predict the type of adsorption process. If the E value is $< 8 \text{ kJ} \cdot \text{mol}^{-1}$, it refers to physical adsorption, $8\text{--}16 \text{ kJ} \cdot \text{mol}^{-1}$ refers to ion exchange, and $> 16 \text{ kJ} \cdot \text{mol}^{-1}$ refers to chemical adsorption takes place.

The estimated values of bonding energy (E) for the present study were found to be $> 16 \text{ kJ/mol}$ for all adsorbent dosage as ($1581\text{--}2886 \text{ kJ} \cdot \text{mol}^{-1}$), which implies that adsorption of chromium ions onto biochar-SO adsorbent

Fig. 11 a PFO, b PSO, c Elovich, d Intraparticle diffusion models of adsorption of Cr^{6+} ions by biochar-SO adsorbent (initial Cr^{6+} ion concentration = $50\text{--}300 \text{ mg} \cdot \text{L}^{-1}$, adsorbent dosage = $2.0 \text{ g} \cdot \text{L}^{-1}$, temperature = 25°C).

is by chemical adsorption. They are chemical species that develop on the adsorbent surface, which are effective in bond formation during a chemical reaction. In the Dubinin-Radushkevich model, the R^2 values ranged from 0.610 to 0.924 for Cr^{6+} by the biochar-SO adsorbent (Table 5).

3.4 Statistical error function analysis of isothermal models

After obtaining the empirical equilibrium data of chromium ions on biochar-SO using Langmuir, Freundlich, Temkin, and D-R isotherm models, several different error functions (hybrid error function) (HYBRID), the root mean square errors (RMS), average percent errors (APE), the sum of the absolute errors (EABS), chi-square error (X^2), and Marquardt's percent standard deviation (MPSD) were used

[60]. The smaller the six error function values expressing the similarity between the experimental data of pea-biochar and the values calculated using theoretical isotherms, this indicates that the model better represents the experimental data (Table 6). The Freundlich model, which has smaller error function values compared to the other models according to the values in Table 6, was determined as the most suitable model for this study.

3.5 Adsorption kinetic studies

For the resulting biochar-SO adsorbents to be considered as candidates for wastewater treatment, a high equilibrium adsorption capacity for a given system must be achieved along with appropriate kinetic parameters. In this study, four

Table 7 PFO and PSO kinetic model results of adsorption of Cr^{6+} ions by biochar-SO adsorbent (initial concentration = (50–300 $\text{mg}\cdot\text{L}^{-1}$), adsorbent dosages = (2.0–6.0 $\text{g}\cdot\text{L}^{-1}$), temperature = (25 °C)

Parameter			PFO			PSO		
Biochar-SO doses ($\text{g}\cdot\text{L}^{-1}$)	Cr^{6+} ion ($\text{mg}\cdot\text{L}^{-1}$)	q_e (exp.)	q_e (calc.)	$k_1 \times 10^3$	R^2	q_e (calc.)	$k_2 \times 10^3$	R^2
2	50	24.68	3.76	6.21	0.956	23.47	14.81	0.999
	75	36.74	5.04	6.21	0.968	35.08	11.36	0.999
	100	45.96	4.34	5.98	0.912	44.44	15.43	1.000
	150	69.86	7.54	6.67	0.738	67.56	8.69	0.999
	200	92.12	9.38	9.44	0.978	90.90	5.14	0.999
	300	135.32	12.45	21.41	0.922	135.14	4.38	0.999
3	50	16.55	1.75	12.66	0.950	16.47	27.41	0.999
	75	24.76	3.26	11.28	0.941	24.51	14.22	0.999
	100	32.48	3.68	6.67	0.939	31.34	16.15	0.999
	150	48.67	5.92	5.52	0.747	46.29	12.37	0.999
	200	62.25	5.47	8.29	0.883	60.97	10.14	0.999
	300	91.41	7.40	11.05	0.910	90.90	6.30	0.999
4	50	12.43	2.06	32.70	0.851	12.54	42.66	0.999
	75	18.66	2.00	13.35	0.974	18.62	23.33	0.999
	100	24.80	3.08	9.67	0.973	24.33	16.07	0.999
	150	37.08	5.30	10.36	0.927	36.36	9.40	0.999
	200	48.35	5.06	7.59	0.939	47.17	11.04	0.999
	300	70.52	4.91	6.67	0.866	68.96	12.66	0.999
5	50	9.96	0.31	3.68	0.028	10.05	69.23	1.000
	75	14.94	1.47	15.43	0.985	14.97	32.21	0.999
	100	19.91	2.41	12.66	0.986	19.80	19.76	0.999
	150	29.85	3.81	11.51	0.964	29.49	12.95	0.999
	200	38.32	4.21	10.82	0.967	37.87	11.53	0.999
	300	56.69	4.32	5.98	0.804	55.24	14.95	0.999
6	50	8.31	0.58	27.40	0.856	8.34	127.90	1.000
	75	12.47	0.97	27.40	0.955	12.54	69.72	1.000
	100	16.61	2.97	35.47	0.990	16.83	27.69	1.000
	150	24.94	3.27	18.19	0.979	25.06	15.56	0.999
	200	33.13	4.41	11.75	0.943	32.78	11.19	0.999
	300	49.52	5.63	8.06	0.899	48.30	9.94	0.999

kinetic models (pseudo–first-order (PFO) kinetic model, pseudo–second-order (PSO) kinetic model, Elovich kinetic model, and intraparticle diffusion) were used to analyze the data obtained on the adsorption of Cr^{6+} ions to biochar-SO as shown in Fig. 11. Values for these models are also summarized in Tables 7–8.

The equilibrium adsorption capacity (q_e) and the rate constant, k_1 , were determined using straight-line plots of $\lg(q_e - q_t)$ versus t (Fig. 11a). The R^2 correlation values (changing between 0.738 and 0.990) of the PFO kinetic model are also illustrated in Table 7 for all adsorbent dosages (2–6 $\text{g}\cdot\text{L}^{-1}$) and beginning Cr^{6+} ion concentrations (50–300 $\text{mg}\cdot\text{L}^{-1}$). Since the R^2 values obtained from Fig. 11a of the PFO kinetic model are relatively low (compared with the PSO kinetic model), this indicates that the evaluated q_e values deviate greatly from the experimental values. When the R^2 correlation coefficients of the

adsorption of Cr^{6+} ions on biochar-SO in Table 7 were examined, no regular increase or decrease in R^2 values was observed with the increase of the adsorbent dosage from 2 to 6 $\text{g}\cdot\text{L}^{-1}$ or the initial Cr^{6+} ion concentration from 50 to 300 $\text{mg}\cdot\text{L}^{-1}$.

The equilibrium adsorption capacity (q_e) and the rate constant, k_2 ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$), are calculated by plotting t/q_e versus t as illustrated in Fig. 11b. The R^2 correlation values of the PSO kinetic model are also illustrated in Table 7 for all adsorbent dosages (2–6 $\text{g}\cdot\text{L}^{-1}$) and beginning chromium ion concentrations (50–300 $\text{mg}\cdot\text{L}^{-1}$). Since the R^2 values obtained from Fig. 11b of the PSO kinetic model are 1, this implies that the calculated q_e values do not deviate from the experimental values. Therefore, the most suitable kinetic model is the PSO kinetic model.

The third model examined, the Elovich model, makes assumptions about the diffusion of gases to heterogeneous

Table 8 Elovich and intraparticle diffusion model results of adsorption of Cr^{6+} ions by biochar-SO adsorbent (initial concentration = (50–300 $\text{mg}\cdot\text{L}^{-1}$), adsorbent dosages = (2.0–6.0 $\text{g}\cdot\text{L}^{-1}$), temperature = (25 ± 2 °C)

Parameter		Elovich			Intraparticle diffusion		
Biochar-SO doses ($\text{g}\cdot\text{L}^{-1}$)	Cr^{6+} ion ($\text{mg}\cdot\text{L}^{-1}$)	β	α	R^2	K_{dif}	C	R^2
2	50	1.12	1E+09	0.935	0.24	20.25	0.943
	75	0.84	4E+10	0.947	0.32	30.80	0.967
	100	0.89	1E+15	0.975	0.29	40.65	0.944
	150	0.42	4E+10	0.853	0.60	59.98	0.769
	200	0.39	4E+13	0.925	0.69	81.38	0.968
	300	0.34	4E+18	0.900	0.80	125.08	0.961
3	50	1.73	7E+09	0.932	0.15	14.50	0.880
	75	1.14	5E+09	0.934	0.24	21.21	0.973
	100	1.05	1E+12	0.949	0.25	28.03	0.951
	150	0.58	5E+09	0.883	0.43	41.04	0.770
	200	0.60	7E+13	0.921	0.43	55.51	0.853
	300	0.54	1E+19	0.850	0.52	83.45	0.931
4	50	2.32	1E+10	0.935	0.11	11.16	0.849
	75	1.79	7E+11	0.936	0.15	16.53	0.979
	100	1.09	1E+09	0.964	0.24	21.12	0.961
	150	0.59	2E+07	0.968	0.44	30.71	0.917
	200	0.68	7E+11	0.965	0.38	42.14	0.912
	300	0.71	1E+19	0.902	0.36	64.38	0.825
5	50	3.43	2E+12	0.899	0.07	9.13	0.797
	75	2.40	7E+12	0.943	0.11	13.43	0.983
	100	1.26	3E+08	0.987	0.21	17.09	0.961
	150	0.76	5E+07	0.981	0.33	25.22	0.917
	200	0.81	1E+11	0.971	0.33	33.49	0.978
	300	0.84	1E+18	0.848	0.30	51.30	0.773
6	50	8.45	2E+27	0.987	0.03	7.92	0.980
	75	3.29	2E+15	0.939	0.07	11.60	0.839
	100	1.44	2E+08	0.965	0.17	14.63	0.884
	150	0.87	2E+07	0.973	0.29	21.37	0.897
	200	0.62	7E+06	0.973	0.41	27.60	0.898
	300	0.57	9E+09	0.959	0.45	42.46	0.895

Table 9 Comparison of the maximum adsorption capacities of Cr^{6+} ions of different adsorbents

Adsorbents	Max. capacity ($\text{mg}\cdot\text{g}^{-1}$)	Max. removal (%)	Ref
Activated carbon from date palm seed	120.48	100	[61]
<i>Eucalyptus globulus</i>	45.00	41	[98]
Fe-doped rice straw biochar	94.95	95	[99]
Wood bark-derived carbon	80.60	90	[100]
Pomegranate husk carbon	35.20	100	[62]
Red alga activated carbon	66.67	59	[65]
γ -Alumina ($\gamma\text{-Al}_2\text{O}_3$)	30.30	70	[101]
Rubber	43.86	100	[102]
<i>Pinus elliottii</i>	10.66	93	[103]
Neem	45.45	95	[104]
Watermelon peel biochar	72.46	69	[29]
Red alga	12.85	58	[65]
Black tea waste	9.14	88	[105]
Biochar-SO	158.73	90.74	This work

surfaces. α ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$) and β ($\text{g}\cdot\text{mg}^{-1}$) in the model refer to the adsorption and desorption rates, respectively. Elovich constant α was calculated from the intercept of Fig. 11c and Elovich constant β was calculated from its slope and is illustrated in Table 5. The R^2 correlation coefficients of the Elovich model are similar to the values of the PFO kinetic model. However, neither model is as suitable for experimental data as the PSO kinetic model (Tables 7–8). The results show that the chemical adsorption during the adsorption of Cr^{6+} ions on the biochar-SO adsorbent can be rate-limiting in some cases. However, the fact that the R^2 values are not very high makes it possible to have physical adsorption in the process.

In addition to the models described above, it is useful to consider the intraparticle diffusion model as it gives an idea about the diffusion mechanism of the system. Adsorption of an adsorbate to an adsorbent takes place in 3 steps:

(i) First, the ions and molecules in the solution adhere to the surface of the adsorbent particles through the liquid film. (ii) The ions and molecules attached to the surface are then diffused into the adsorbent. (iii) A chemical reaction takes place very quickly in the active groups of the adsorbent particles. In determining the adsorption rate, the step with the slowest speed from these three steps is taken as a basis. If the lines obtained according to Fig. 11d pass through the origin, this shows that the adsorption process is controlled by the intraparticle diffusion step by Weber and Morris [93]. As seen in Fig. 11d, in cases where the lines do not pass through the origin, that is, the C values are large, the rate of the adsorption process is determined by the film diffusion. This can be explained by the decrease in Biochar-SO pore volume and surface area overtime during the adsorption process. The C and K_{dif} values shown in Table 8 were evaluated from the intercept point and slope of the plot of q_t versus $t^{0.5}$, respectively. When the C values of the adsorption of Cr^{6+} ions on biochar-SO in Table 8 were examined, a regular increase in C values was observed with the increase of the adsorbent dose from 2.0 to 6.0 $\text{g}\cdot\text{L}^{-1}$ or the initial Cr^{6+} ion concentration from 50 to 300 $\text{mg}\cdot\text{L}^{-1}$.

3.6 Comparison with results reported in the literature

In the literature review summarized in Table 9, the effectiveness of the elimination of chromium ions using alternative adsorbents was compared with the biochar-SO and showed that biochar-SO was potent in removing chromium ions.

3.7 Regeneration of biochars

It is a widely used method for the removal of pollutants from wastewater that relies heavily on the reuse of adsorbent materials, and the economics of this technology is highly dependent on the reuse of these adsorbent materials as well. For the regeneration of depleted biochar-SO, a

Fig. 12 The regeneration cycles effect for **a** desorption percentage of Cr^{6+} ions from biochar-SO, **b** adsorption percentage of Cr^{6+} ions on biochar-SO using 3 $\text{g}\cdot\text{L}^{-1}$ of adsorbent dose and 2 $\text{g}\cdot\text{L}^{-1}$ initial concentration of Cr^{6+} ions at $25 \pm 2^\circ\text{C}$

chemical regeneration process is employed. The biochar-SO was regenerated by washing it with 0.1-N NaOH solution, 0.1-M HCl solution, and then hot pure water, followed by drying it. It was discovered that the highest removal of Cr^{6+} ions by biochar-SO was 90% after six regeneration cycles, respectively (Fig. 12), demonstrating that biochar-SO can regenerate.

4 Conclusion

This study showed that pea peels, which are agricultural waste, can be used as inexpensive and effective biochar. Biochar-SO produced from pea peels was used for the elimination of Cr^{6+} ions from wastewater. It has been understood that solution pH, adsorbent dosage, initial concentration of Cr^{6+} ions, and adsorption time are effective parameters in the adsorption process of chromium ions onto prepared biochar-SO. For the elimination of chromium ions using biochar-SO, it was determined that the highest Cr^{6+} removal (90.74%) occurred at pH 1.48. Biochar adsorbent with $6 \text{ g}\cdot\text{L}^{-1}$ concentration had minimum adsorption amount (q_e) at equilibrium and maximum removal percentage in removing Cr^{6+} ions. It has been determined that the Freundlich isotherm model in the elimination of chromium ions on biochar-SO is in perfect agreement with the experimental data ($R^2 = 1$). Although the sorption of Cr^{6+} ions onto biochar-SO adsorbent was better described by the Freundlich model, the maximum adsorption capacity calculated by using the Langmuir isotherm as $158.73 \text{ mg}\cdot\text{g}^{-1}$. Estimated binding energy (E) values ($1581\text{--}2886 \text{ kJ}\cdot\text{mol}^{-1}$) obtained from Dubinin-Radushkevich isotherm models for this study show the chemical adsorption structure as it is considerably larger than $16 \text{ kJ}\cdot\text{mol}^{-1}$. In conclusion, we believe that biochar-SO obtained from pea peels may be successfully used to purify wastewaters containing toxic Cr^{6+} ions.

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Data availability Data sharing is not applicable to this article.

Declarations

Consent to participate Not applicable.

Conflict of interest The authors declare no competing interests.

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