Application of Response Surface Methodology and Artificial Neural Network for The Preparation of Fe-Loaded Biochar for Enhanced Cr(VI) Adsorption and Its Cr(VI) Adsorption Characteristics in an Aqueous Solution

Jin-Kyu Kang  
Pusan National University

Eun-Jin Seo  
Hankyong National University

Chang-Gu Lee  
Ajou University

Sanghyun Jeong  
Pusan National University

Seong-Jik Park (parkseongjik@hknu.ac.kr)  
Hankyong National University  https://orcid.org/0000-0003-2122-5498

Research Article

Keywords: food waste, biochar, iron loading, hexavalent chromium, response surface methodology, artificial neural network

Posted Date: January 28th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1209744/v1

License: ☁️  This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

In this study, we optimized and explored the effect of the conditions for synthesizing Fe-loaded food waste biochar (Fe@FWB) for Cr(VI) removal using the response surface methodology (RSM) and artificial neural network (ANN). The pyrolysis time, temperature, and Fe concentration were selected as the independent variables, and the Cr(VI) adsorption capacity of Fe@FWB was maximized. RSM analysis showed that the p-values of pyrolysis temperature and Fe concentration were less than 0.05, indicating that those variables were statistically significant, while pyrolysis time was less significant due to its high p-value (0.2830). However, the ANN model results showed that the effect of pyrolysis time was more significant on Cr(VI) adsorption capacity than Fe concentration. The optimal conditions, determined by the RSM analysis with a lower sum of squared error than ANN analysis, were used to synthesize the optimized Fe@FWB (Fe@FWB-OPT) for Cr(VI) removal. From the equilibrium model fitting, the Langmuir model showed a better fit than the Freundlich model, while the Redlich–Peterson isotherm model overlapped. The Cr(VI) sorption capacity of Fe@FWB-OPT calculated from the Langmuir model was 377.71 mg/g, high enough to be competitive to other adsorbents. The kinetic Cr(VI) adsorption was well described by the pseudo-second-order and Elovich models. The XPS results showed that Cr adsorbed on the surface of Fe-FWB-OPT was present not only as Cr(VI) but also as Cr(III) by the reduction of Cr(VI). The results of Cr(VI) adsorption by varying the pH indicate that electrostatic attraction is a key adsorption mechanism.

1. Introduction

Chromium (Cr) is widely used as a corrosion inhibitor, catalyst, and fungicide to produce stainless steel, pigments, wood preservatives, and tanning (Christensen 1995). The chemical, metallurgical, and refractory industries are the main sources of Cr discharge into the environment in the form of metal-containing dust, vapors, fumes, and wastewater (Keegan et al. 2008). Cr has several oxidation states, wherein Cr(VI) and Cr(III) are the dominant Cr species that exist in the environment (Rowbotham et al. 2000, Yoshinaga et al. 2018). Cr(VI) is known to be more toxic than Cr(III) (Rowbotham et al. 2000). Cr(VI) poses a threat to human health by causing skin lesions, ulceration and perforation of the nasal septum, eardrum perforation, decreased spermatogenesis, and lung carcinoma (Bharagava &Mishra 2018, Mishra &Bharagava 2016). The International Agency for Research on Cancer (IARC) classified Cr(VI) as a Group 1 carcinogen (carcinogenic for humans) (Yoshinaga et al. 2018), and the World Health Organization (WHO) sets 50 mg/L of Cr as the standard concentration permissible for drinking water (World Health 2017).

Various techniques, including adsorption, membrane filtration, ion exchange, and electrochemical treatment, have been applied to remove Cr(VI) from domestic and industrial wastewater (Owlad et al. 2009). Adsorption is superior to other technologies because of its low cost, ease of operation, high efficiency, and availability, and it has great advantages in terms of economy and environment (Owlad et al. 2009). Despite being a well-established technology, many researchers are still conducting studies to find an adsorbent that is more efficient. Various natural and synthetic materials have been used as Cr(VI) removal adsorbents, including activated carbons, bio-derived materials, zeolites, natural clays, and industrial waste (Owlad et al. 2009).

Biochar is also a promising adsorbent for the removal of contaminants from water and wastewater because of its high porosity, low cost, environmental friendliness, high stability, surface functional groups, and accessible synthesis methods (Mei et al. 2020). However, unmodified biochar has a lower adsorption capacity, especially for anions, such as selenate, fluoride, arsenate, and phosphate. Impregnating metal salts to biochar has been applied to improve the adsorption performance of biochar by pretreating biochar with an inorganic material before pyrolysis (Wei et al. 2018). After pyrolysis, these inorganic metal salts adhere to the surface of the biochar via the formation of metal oxide nanoparticles, thus improving the adsorption capacity of the biochar (Tan et al. 2016). Previous studies have reported that metal-impregnated biochar is effective for anions, such as selenate (Hong et al. 2020, Lee et al. 2021), fluoride (Mei et al. 2020, Mei et al. 2021), arsenate (Lyonga et al. 2020), chromate (Dong et al. 2011), and phosphate (Kang et al. 2021). Food waste (FW), separately collected at the household level in Korea, can be used more efficiently for biochar production than sewage sludge with hazardous heavy metals (Hong et al. 2020). The utilization of the pyrolysis byproduct is an environmentally friendly option because pyrolysis is an effective way to reduce not only the FW and generate combustible gases such as H₂, CO, and CH₄ (Lee et al. 2020).

Most previous studies have been performed based on a simple experimental design in which one parameter is varied while the other parameters are kept constant. This conventional method requires many experimental runs and enables the investigation of the effects of interactions between two or more variables, leading to a high consumption of time and chemicals and inaccurate prediction (Khayet et al. 2010, Park &An 2016). Response surface methodology (RSM) can be used to apply the experimental design without such limitations. RSM analyzes the various independent variables influencing the dependent variables in one system with multiple experimental runs. The results obtained from RSM enable the elucidation of the optimized conditions and the evaluation of the relative significance of several factors, even in the presence of complex interactions (Montgomery 2017, Myers et al. 2016). An artificial neural network (ANN) is also suggested to solve the non-linear relationships between multiple input and output variables in complex systems (Yetilmezsoy &Demirel 2008). The ANN is an artificial intelligence technique that mimics the human brain's biological neural network in problem-solving processes, and the prediction with ANN is made by learning the experimentally generated data or using validated models (Turan et al. 2011).

In this study, Fe-loaded food waste biochar (Fe@FWB) was evaluated as an adsorbent for removing Cr(VI) from wastewater. To the best of our knowledge, the removal of Cr(VI) using Fe@FWB has not been previously studied. The pyrolysis time, temperature, and Fe concentration were selected as the conditions for optimizing the production of Fe@FWB, and their effects on the Cr(VI) adsorption capacity of Fe@FWB were explored using RSM and ANN. The Fe@FWB synthesized under optimized conditions using RSM (Fe@FWB-OPT) was analyzed with respect to its physicochemical properties and Cr(VI) adsorption characteristics, and these results were used to elucidate the Cr(VI) adsorption mechanisms.

2. Materials And Methods

2.1. Biochar preparation and modification
Fe@FWB was prepared as described in our previous study (Hong et al. 2020). FW was supplied by a food waste treatment plant located in Seoul, South Korea. FW collected from the household level was dehydrated using a steam boiler at 150°C. Magnet and trommel separators were used to isolate foreign substances, such as iron, in dried FW. The FW was dried in a drying oven at 80°C for 24 h. Fe loading was performed by mixing 300 mL of 0.1, 0.3, and 0.5 M FeCl$_3$ solution with 100 g of dried FW for 24 h. The mixture of FeCl$_3$ solution and FW was re-dried at 80°C for 36 h before pyrolysis. Pyrolysis was performed in a stainless-steel muffle furnace at various temperatures (300, 450, and 600°C) and times (1.0, 2.5, and 4.0 h). The preparation of the mixture and the pyrolysis conditions were designed using a Box-Behnken model, a type of RSM. The heating rate and pyrolysis atmosphere were fixed at 10°C/min, and N$_2$ was continuously flowed into the furnace to maintain anoxic conditions. The pyrolyzed and cooled Fe@FWB was stored in a desiccator to prevent the adsorbent from oxidation and moisture absorption.

2.2 Exploring the optimal Fe@FWB pyrolysis conditions and investigating the significance of parameters for Cr(VI) adsorption capacity using response surface methodology and artificial neural network

The conditions for the Fe@FWB precursor and pyrolysis were coded using the Box-Behnken model (Table S1). Seventeen sets of experimental runs were performed to quantify the Cr(VI) adsorption capacity of Fe@FWB synthesized under different conditions. The relationship between the three input variables and response variable was analyzed using RSM and ANN.

The optimization of the RSM consists of a cubic equation (Eq. 1) was performed using Design-Expert 10 (STAT-EASE Inc., Minneapolis, MN, USA):

\[
Y = a_0 + \sum_{i=1}^{3} a_i X_i + \sum_{i=1}^{3} \sum_{j=1}^{3} a_{i,j} X_i X_j + \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=1}^{3} a_{i,j,k} X_i X_j X_k
\]

where $Y$ is the predicted Cr(VI) adsorption capacity of Fe@FWB (mg-Cr(VI)/g), $a_0$ is the constant coefficient, $X_i$ is the independent coded level, and $a_i$ is the coefficient parameter, while $i = 1, 2, 3$ are the pyrolysis time, pyrolysis temperature, and Fe concentration, respectively.

The optimization of the feed-forward ANN was performed using the neural network tool (nntool) of Matlab 2021a (Mathworks, Massachusetts, USA). The input layer was compositied with the corresponding input variable values. The optimum ANN structure was determined by varying the number of neurons in the hidden layer. The number of neurons in the hidden layer was varied from 3 to 12 (topology: 3:3:1–3:12:1), while the transfer function was a hyperbolic tangent sigmoid transfer function (tansig). The output layer was the one variable for Cr(VI) adsorption capacity (mg/g) of Fe@FWB, while the transfer function was a linear transfer function (purelin). The transfer functions and ANN model used in this study can be described as follows:

\[
tansig(x) = \frac{2}{1 + e^{-2x}} - 1
\]

\[
\text{purelin}(x) = x
\]

\[
\begin{bmatrix}
h_{1,1} \\
\vdots \\
h_{1,j}
\end{bmatrix} = \text{tansig}
\begin{bmatrix}
w_{1,1} \\
\vdots \\
w_{1,j}
\end{bmatrix} \times
\begin{bmatrix}
X_1 \\
X_2 \\
X_3
\end{bmatrix} +
\begin{bmatrix}
b_{1,1} \\
\vdots \\
b_{1,j}
\end{bmatrix}
\]

\[
Y = \text{purelin}
\begin{bmatrix}
w_{2,1} \\
\vdots \\
w_{2,1}
\end{bmatrix} \times
\begin{bmatrix}
h_{1,1} \\
\vdots \\
h_{1,j}
\end{bmatrix} +
\begin{bmatrix}
b_{2,1} \\
\vdots \\
b_{2,1}
\end{bmatrix}
\]

In the nntool, the experimental set was divided randomly into a training set (60%), a validation set (20%), and a test set (20%). At this time, because there are only 17 experimental conditions, dividing them into three sets is likely to reduce the representation of the data contained in each set, and the ANN optimization is also challenging. Therefore, in this work, we cloned 17 datasets to create 34 datasets and utilize them for ANN optimization. The least mean squared error (MSE) value for the validation set was determined by adjusting the value of the weight set ($\overline{w}$) and bias set ($\overline{b}$) for the ANN optimization. However, the data included in the validation set varied with topology. Therefore, the best topology and its $\overline{w}$ and $\overline{b}$ were chosen from the highest correlation coefficient ($R$) from all the data.

2.3. Analysis of the physical and chemical properties of optimized Fe@FWB before and after Cr(VI) adsorption

Various types of equipment were used to investigate the physicochemical properties of the optimized Fe@FWB (Fe@FWB-OPT) and Cr(VI)-adsorbed Fe@FWB-OPT. The surface morphology and elemental composition were investigated using field-emission scanning electron microscopy (FE-SEM) (Sigma, Carl Zeiss, Germany) and energy-dispersive X-ray spectroscopy (EDS). The specific surface area, pore volume, and pore size of the Fe@FWB-OPT were determined by applying the BET and BJH models to the N$_2$ adsorption-desorption isotherms obtained from an Autosorb-iQ 2ST/MT analyzer (Quantachrome, USA). The samples for the analysis of the specific surface area and pore size distribution were pretreated by outgassing at 80°C combined with a vacuum at $10^{-9}$ bar for 12 h. Fourier transform infrared spectroscopy (FTIR) spectra were used to investigate the functional groups of Fe@FWB-OPT and Cr(VI)-adsorbed Fe@FWB-OPT. The KBr pellet technique was used for the sample preparation. The FTIR spectra were recorded at room temperature using a Nicolet 6700 spectrometer (Thermo Fisher Scientific, United Kingdom) in the range of 4000 to 500 cm$^{-1}$ at a 4 cm$^{-1}$ of nominal spectral resolution. The chemical characteristics and Cr(VI) removal mechanism were also examined by X-ray photoelectron spectroscopy (XPS, K-Alpha*, Thermo Fisher Scientific, United Kingdom) with Al K$_\alpha$ radiation (hv = 1253.6 eV).
2.4. Adsorption experiments for the optimization of Fe@FWB and exploration of Cr(VI) adsorption characteristics by Fe@FWB-OPT

The batch experiments quantified the Cr(VI) adsorption capacities of Fe@FWB synthesized under different preparation conditions designed by RSM. All of the batch experiments were conducted by following conditions (unless otherwise stated): 0.1 g of Fe@FWB was reacted with 30 mL of 500 mg/L Cr(VI) solution in a 50 mL conical tube by a shaking incubator (SJ-808SF; Sejong Scientific Co., Korea) at 100 rpm and 25°C. The Cr(VI) stock solution (1000 mg Cr (VI)/L) was prepared by dissolving potassium dichromate (K2Cr2O7) in deionized (DI) water, and the stock solution was diluted with DI water to prepare the Cr(VI) solution at a specific concentration. The reacted solutions and Fe@FWB were parted by using a 0.45 μm GF/C filter, and the Cr(VI) concentration was determined using a UV-visible spectrophotometer (Optizen, Mecasys Corporation, Korea) at 540 nm. The experiments were performed three times to ensure the reliability and consistency of the data.

Fe@FWB-OPT synthesized under optimized conditions was used for further batch experiments, including initial Cr(VI) concentration, reaction time, temperature, initial pH, and competing anions. The Cr(VI) adsorption to Fe@FWB-OPT was quantified by varying the initial Cr(VI) concentration from 50 to 3000 mg Cr (VI)/L at a fixed reaction time of 24 h to obtain the Cr(VI) adsorption isotherm. A Cr(VI) solution of 500 mg Cr (VI)/L was also reacted with Fe@FWB-OPT for 15 min to 24 h to investigate the effect of the reaction time on Cr(VI) adsorption. The Cr(VI) adsorption was also quantified at different reaction temperatures (15, 25, and 35°C) to explore the thermodynamic characteristics of Cr(VI) adsorption by Fe@FWB-OPT. The equilibrium, kinetic, and thermodynamic adsorption data were analyzed using the mathematical equations provided in the supplementary information to investigate the Cr(VI) adsorption characteristics. pH experiments were performed by reacting Cr(VI) solution with Fe@FWB-OPT under different initial pH values ranging from pH 3 to 11 using 0.1 M HCl and 0.1 M NaOH. The pH of the solution was measured using a pH meter (Seven-multi S40; Mettler Toledo, Switzerland). Furthermore, the effect of competing oxyanions was evaluated by reacting the competing oxyanion-containing Cr(VI) sorption and Fe@FWB-OPT for 24 h. To investigate the influence of the presence of anions including phosphate, bicarbonate, sulfate, and nitrate, 1 and 10 mM of Na3HPO4, NaHCO3, Na2SO4, and NaNO3 were dissolved in 500 mg/L of Cr(VI) solution, respectively, and each solution was reacted with Fe@FWB-OPT for 24 h.

3. Results And Discussion

3.1. Response surface methodology and artificial neural network application for the optimization of Fe@FWB for Cr(VI) removal

The experimental conditions for Fe@FWB were derived from the Box–Behnken design, including 17 experimental conditions with five central points. From a statistical design, such as the Box–Behnken design, the effect of each variable can be examined evenly. By applying RSM, it is possible to find optimized conditions and evaluate the relative significance of several factors (Kim et al. 2019, Myers et al. 2016). The optimized cubic order model, which was obtained using Design-Expert statistical software, is presented as follows:

\[
Y = 16.62 + 0.29X_1 - 14.28X_2 + 5.90X_3 + 3.46X_1X_2 + 0.26X_1X_3 - 4.60X_2X_3 - 0.98X_1^2 + 9.56X_2^2 - 7.00X_3^2 - 5.40X_1^2X_2 - 3.16X_1^2X_3 - 3.75X_1X_2X_3
\]

Design-Expert statistical software also provided the analysis of variance (ANOVA) results (Table 1). The model F-value, calculated by dividing the mean squares of each variable effect by the mean square, was 1250.22. This large value indicates the importance of the regression model (Hemmat Esfe et al. 2018). Terms with a p-value less than 0.05 were considered significant. The determination coefficient (R²) and adjusted R² (R²adj) were 0.9997 and 0.9989, respectively, indicating the high suitability of the RSM prediction. The p-values of X2 and X3 were less than 0.05 (<0.001), while the p-value of X1 was 0.2830. The pyrolysis temperature and Fe concentration were statistically significant, and the pyrolysis time was less significant. These results were also observed in our previous study (Hong et al. 2020). However, other terms containing X1, (X1X2, X1X3, X2X3, X1X2X3, X12, X1X2X) exhibited relatively low p-values (< 0.05), except for the X1X2 term. Therefore, the pyrolysis time may also be significant when its effects are combined with other variables. The coefficient of X2, which is negative and has the largest absolute value, assumes that the smaller the pyrolysis temperature, the greater the Cr(VI) adsorption. In the case of X3, the terms containing X3 have different signs, indicating that the Fe concentration effects are significantly affected by the other conditions.
Table 1
Analysis of variance results for the RSM prediction of Cr(VI) adsorption capacity of Fe@FWB synthesized under different experimental conditions designed by RSM

| Source       | Sum of Squares | df | Mean Square | F Value | p-value | Prob > F |
|--------------|----------------|----|-------------|---------|---------|---------|
| Model        | 3279.93        | 12 | 273.33      | 1250.23 | < 0.0001|         |
| $X_1$        | 0.34           | 1  | 0.34        | 1.54    | 0.2830  |         |
| $X_2$        | 815.49         | 1  | 815.49      | 3730.14 | < 0.0001|         |
| $X_3$        | 139.05         | 1  | 139.05      | 636.04  | < 0.0001|         |
| $X_1X_2$     | 47.76          | 1  | 47.76       | 218.45  | 0.0001  |         |
| $X_1X_3$     | 0.26           | 1  | 0.26        | 1.19    | 0.3359  |         |
| $X_2X_3$     | 84.68          | 1  | 84.68       | 387.35  | < 0.0001|         |
| $X_1^2$      | 4.06           | 1  | 4.06        | 18.57   | 0.0126  |         |
| $X_2^2$      | 385.13         | 1  | 385.13      | 1761.65 | < 0.0001|         |
| $X_3^2$      | 206.05         | 1  | 206.05      | 942.48  | < 0.0001|         |
| $X_1^2X_2$   | 58.27          | 1  | 58.27       | 266.52  | < 0.0001|         |
| $X_1^2X_3$   | 19.97          | 1  | 19.97       | 91.34   | 0.0007  |         |
| $X_2^2X_2$   | 28.05          | 1  | 28.05       | 128.30  | 0.0003  |         |
| Residual     | 0.87           | 4  | 0.22        | 0.34    |         |         |
| Cor. Total   | 0.34           | 1  | 0.34        |         |         |         |

From the optimized ANNs, the MSE from the validation set and $R$ from all data set are presented in Table S2. ANN with the topology 3:11:1, the smallest MSE for validation set and the highest $R$ value for all data, was selected as the most optimal ANN for predicting the Cr(VI) adsorption capacity of Fe@FWB. The $\vec{w}$ and $\vec{b}$ for topology 3:11:1 are presented in Table 2.

Table 2
Values of weights and biases for topology 3:11:1

| n  | $w_{1,n}$ | $b_{1,n}$ | $w_{2,n}$ | $b_{2,n}$ |
|----|-----------|-----------|-----------|-----------|
|    | $i=1$     | $i=2$     | $i=3$     | $i=1$     | $i=2$     | $i=3$     | $i=1$     | $i=2$     | $i=3$     | $i=1$     | $i=2$     | $i=3$     |
| 1  | -0.32609  | -3.2709   | 0.20127   | 2.8662    | -0.15922  | -0.41816  |
| 2  | 0.62022   | -3.0789   | 0.31602   | -2.2892   | -0.28391  |
| 3  | -1.3703   | 2.1073    | -1.7578   | 1.7697    | 0.01867   |
| 4  | 0.70406   | -3.0881   | 0.053081  | -1.0988   | 0.6863    |
| 5  | 1.1724    | 2.7922    | 0.83393   | -0.60115  | -0.48486  |
| 6  | -2.0521   | 1.7351    | 1.5268    | 0.93478   | 0.13787   |
| 7  | -3.0715   | -0.27869  | -0.94002  | -0.59158  | -0.6173   |
| 8  | -2.7838   | 0.57864   | -1.6854   | -1.1114   | 0.57654   |
| 9  | -0.42836  | -1.0333   | 2.7296    | -2.1135   | 0.086333  |
| 10 | -0.42967  | -0.40517  | -2.9931   | -2.5684   | -0.53938  |
| 11 | 0.72255   | 2.5915    | 1.9263    | 2.9177    | -0.30494  |

From the weight values, the effect of each variable on the output was calculated as follows:

$$ E_i = \frac{\sum_{j=1}^{11} \left( |w_{1,n}| \times |w_{2,n}| \right)}{\sum_{j=1}^{3} \left( \sum_{n=1}^{11} \left( |w_{1,n}| \times |w_{2,n}| \right) \right)} \times 100(\%) \quad (6) $$

Page 5/15
where $E_i$ is the effect of each variable on the output (%). $i = 1, 2, 3$ are $X_1$, $X_2$, and $X_3$. Several studies have reported that the order of $E_i$ is the same as the significance order from the ANOVA results obtained from RSM [27, 28]. In this study, however, the order and values of $E_i$ were $39.4% \ (X_2) > 32.6% \ (X_3) > 28.0% \ (X_3)$, which differs from the order of the RSM analysis ($X_2 > X_3 > X_1$). This difference is considered to be due to the structural characteristics of the RSM and ANN.

The RSM used in this study is a cubic order-based model, and the suitability of the cubic order means that each variable does not affect the response independently. Therefore, it was difficult to determine whether the $p$-value from the first-order term directly indicates each variable's importance and order. In contrast, $E_i$ is calculated from the weight values of the ANN model, while ANN is a type model in which each variable is connected in a complex manner. Therefore, while the $E_i$ value has less statistical significance, it can be used to indirectly compare the influence of a specific variable in the ANN model in which each variable acts in combination. Therefore, ANOVA analysis through RSM is suitable for evaluating the effect when each variable acts individually or in combination, and the calculation of $E_i$ through ANN is suitable for evaluating the overall effect of each variable. Based on these characteristics, if the two models are used simultaneously, complementary results could be obtained when evaluating the influence of factors. In both models, the pyrolysis temperature ($X_2$) was judged to be the most significant variable, and the pyrolysis time ($X_1$) and Fe concentration ($X_3$) were less important. At this time, the pyrolysis time ($X_1$) is judged to have a more significant influence when acting with variables other than acting individually. Zhang and Pan (2014) also reported an indirect relationship between the ANOVA result from RSM and the $E_i$ values from the ANN. In their study, the term for pyrolysis temperature in the ANOVA result from RSM was insignificant ($p = 0.9969$), but $E_i$ for temperature still showed 13.39% from the significance of other terms containing temperature. Jang et al. (2020) also reported that the $E_i$ order was pH (48.2%) > initial adsorbate concentration (29.3%) > adsorbent dosage (22.5%), while the significance order of first-order variables from ANOVA was pH $\geq$ adsorbent dosage $>$ initial adsorbate concentration.

From the RSM and ANN, the regression graph of the observed and model-predicted Cr(VI) adsorption capacity of Fe@FWB is presented in Figure 1. Both RSM and ANN showed predictive results that were almost consistent with the observed values, and the results predicted by the two models confirm that there is no significant difference (Figure 1). $R^2$ and $SSE$ confirm that both models show near-consistent predictive properties, however, the $SSE$ from RSM was slightly lower than that of ANN. When the Cr(VI) adsorption capacities of Fe@FWB expected by the two different models were compared, the predicted results from the two models showed similar trends according to the change in independent variables. However, they also differed noticeably in their predictions of points that were not actually utilized for optimization (Figure 2). As shown in Figure 2, the predictions by RSM, which were developed using differentiable cubic equations, showed a smoother form of results compared to ANNs. However, a model with smoother graphs does not indicate that the model predicts the experimental data more accurately.

The optimal conditions that showed the maximum response and the Cr(VI) adsorption capacity of Fe@FWB were tracked using RSM and ANN. As a result, 53.52 and 52.95 mg/g were obtained under pyrolysis time: pyrolysis temperature: Fe concentration = 1.0 h : 300°C : 0.42 M for RSM and 1.0 h : 300°C : 0.26 M for ANN, respectively. The Cr(VI) adsorption amount of Fe@FWB expected from RSM was slightly higher than that of ANN. The optimal conditions obtained from the two models were equal in terms of pyrolysis time and temperature, with differences in Fe concentrations. In this work, we synthesized Fe@FWB-OPT based on the optimal synthesis conditions obtained through RSM because RSM showed slightly higher accuracy (higher $R^2$ and lower $SSE$ value) and higher Cr(VI) adsorption capacity than ANN. Further batch experiments were performed using Fe@FWB prepared under optimized conditions from RSM (Fe@FWB-OPT).

### 3.2. Characteristics of Fe@FWB-OPT before and after Cr(VI) adsorption and its mechanism study

From the FE-SEM results, Fe@FWB-OPT had a smooth surface without pores developed by pyrolysis (Figure S1). Because pyrolysis was performed at a relatively low temperature after Fe loading, the pores were developed. No crystals were observed on the surface of Fe@FWB-OPT, indicating that Fe was uniformly distributed. The Fe content was high (24.2%), indicating that the loaded Fe was fixed on FWB after pyrolysis (Table S3).

The specific surface area, pore volume, and pore size of Fe@FWB-OPT are listed in Table S3. The pore size distribution and accumulative pore volume obtained from the BJH plot are presented in Figure S2. The pores mainly consisted of $<35$ nm pore diameter and 0.0083 cm$^3$/g accumulative volume, and the accumulative pore volume also increased to 0.0103 cm$^3$/g when the pore diameter increased from 35 to 171 nm. Even though Fe@FWB-OPT has mesopores and micropores, the specific surface area was 4.144 m$^2$/g. This is consistent with the poor development of pores on the surface of Fe@FWB-OPT, as observed by FE-SEM.

The FTIR spectra of Fe@FWB-OPT before and after Cr(VI) adsorption are shown in Figure S3. There were no noticeable differences in the FTIR spectra due to the adsorption of Cr(VI). Although the peaks at 1000–700 cm$^{-1}$ are known to be associated with Cr(VI) (Cheng et al. 2011, Lin et al. 2019), several studies have been unable to find the new peak by Cr(VI) when comparing before and after Cr(VI) adsorption. Although these studies described the adsorption of Cr(VI) as the shift of some functional groups (Espinoza-Sánchez et al. 2019, Hong et al. 2008, Huang et al. 2014, Karthik & Meenakshi 2015, Srivastava et al. 2015, Zhao et al. 2021), this type of shift was not observed in the present study due to the fact that Cr(VI) adsorption through reaction with Fe was the primary mechanism. The peaks at 3400 and 1630 cm$^{-1}$ were attributed to the stretching of O-H or scissors-bending of O-H-O of water molecule (Mojet et al. 2010). The peaks at 2922 and 2850 cm$^{-1}$ correspond to C-H stretching (Simons 1978). The peaks at 1419 cm$^{-1}$ correspond to the asymmetric bending of CH$_2$ or in-plane bending of O-H (Coates 2006, Simons 1978). The peaks at 1160 and 1040 cm$^{-1}$ were attributed to the vibrations of skeletal C-C (Coates 2006). Therefore, Fe@FWB-OPT is considered to be a single-bonded carbon material.
The XPS spectra and deconvoluted results of Fe@FWB-OPT and Cr(VI)-adsorbed Fe@FWB-OPT are presented in Figure 3. The main of C1s is deconvoluted as C-C and C-O at 284.6 and 285.4 eV, respectively, and the smaller peak is considered as C=O at 288.5 eV, which is similar to the reported C1s deconvolution of biochar, while there has no specific change or shift after Cr(VI) adsorption (Hu et al. 2019, Puziy et al. 2008, Reguyal & Sarmah 2018, Terzyk 2001). The O1s peak was also considered to be a combination of C=O at 531.6 eV and C-O or inorganic oxygen bonded to Fe at 532.5 eV (Hu et al. 2015, Llorens et al. 2015). However, there was no significant change before and after adsorption in O1s, which indicates that Cr(VI) was not adsorbed by ligand exchange with the OH of Fe-OH. From the Fe2p spectra, the Fe2p$_{3/2}$ peak is deconvoluted as the contribution of Fe$^{2+}$, Fe$^{3+}$, and FeOH at 709.8, 711.3, and 713.1 eV (Ding et al. 2015). After Cr(VI) adsorption, the peak of FeOH did not change noticeably, and the peak of Fe$^{2+}$ decreased, while the peak of Fe$^{3+}$ increased. The change in Fe2p also suggests that some part of Cr(VI) was adsorbed by reduction to Cr(III), followed by Cr(III) adsorption by reacting with Fe$^{2+}$ was followed. The Cr2p spectrum of Cr(VI) adsorbed Fe@FWB-OPT is deconvoluted as Cr(III) at 576.8 and 586.7 eV and Cr(VI) at 579 eV (Lu et al. 2021). The Cr2p spectrum indicates that the adsorbed chromium is adsorbed not only as Cr(VI) but also as Cr(III) after the reduction of Cr(VI).

### 3.3. Effect of initial Cr(VI) concentration

Cr(VI) adsorption to Fe@FWB-OPT was quantified under different initial concentrations. The adsorbed amount of Cr(VI) is presented in Figure S4 as a function of the equilibrium concentration with the three different model fits. The fitted model parameters are presented in Table S4. The Cr(VI) adsorbed amounts by Fe@FWB-OPT continued to increase as the initial concentration of Cr(VI) increases, and the Cr(VI) adsorption capacity reached 188.97 ± 9.74 mg/g when the equilibrium Cr(VI) concentration was 2370.11 ± 26.52 mg/L.

The Freundlich, Langmuir, and Redlich-Peterson models were used as equilibrium models (SI). If $g$ is 1, the Redlich–Peterson model is reduced to the Langmuir model, and if $gC_e^a$ is much larger than 1, the Redlich–Peterson model will be deducted to the Freundlich model (Wu et al. 2010). Because the Redlich–Peterson model contains both Langmuir and Freundlich models, the Redlich–Peterson model would fit best if the adsorption response falls between the trends shown by both models (Belhachemi & Addoun 2011). Based on $R^2$, $\chi^2$, and SSE in Table S4, the Langmuir and Redlich–Peterson models were more suitable for describing the data obtained from adsorption isotherm experiments than the Freundlich model. The $g$ value of 1 also supports this result. Therefore, Cr(VI) adsorption on Fe@FWB-OPT was considered to be monolayer adsorption (Swenson & Stadie 2019).

The maximum adsorption capacity ($Q_m$) of Fe@FWB-OPT, obtained from the Langmuir model, was 377.71 mg/g. This value is relatively large compared to studies in which Cr(VI) was removed using biochar (Table 3). Furthermore, it is significant that this high value has been obtained at neutral pH compared to the relatively low pH (mostly pH 2) of other studies. Furthermore, Fe@FWB-OPT was granular in size (0.425 mm), enabling easy separation of the adsorbent from the solution after Cr(VI) removal.
3.6. Effect of solution chemistry on Cr(VI) adsorption

The 

increase from 33.09 ± 1.82 mg/g to 53.85 ± 0.57 mg/g. This result is consistent with the positive thermodynamic equations (provided in SI) are provided in Table S7. By increasing the temperature from 15°C to 35°C, the Cr(VI) adsorption capacity also increased with the intercept of the regression equation of the first step was 0 mg/g and the regression lines passed through the origin, indicating that diffusion is a rate-limiting step for Cr(VI) adsorption (Pholosi et al. 2020). The overall adsorption rate is well fitted to the Cr(VI) adsorption kinetics on Fe@FWB-OPT when the steps were divided at a turning point of 2 h. With the appropriate description by pseudo-second-order and Elovich models, the adsorption rate at the initial stage was considered diffusion-limited. The sorption capacities for each step were 27.51 ± 0.64 and 49.76 ± 1.40 mg/g. The results of the reaction time and fitted data using the kinetic models are shown in Figure S5. Cr(VI) adsorption can be divided into two steps: the immediate reaction kinetics is not governed by first- or second-order reactions, pseudo-first-order and pseudo-second models are widely used to predict the adsorption kinetics (Simonin 2016). The Elovich model was derived from the assumption that adsorption proceeds on heterogeneous surfaces without desorption (Wu et al. 2009). Furthermore, the intra-particle diffusion model, which considers intra-particle diffusion as a rate-limiting step, was also employed (Weber &Morris 1963). The model fitted parameters and model accuracy indicators, including $R^2$, $\chi^2$, and the sum of squared errors (SSE), are listed in Tables S5 and S6. From $R^2$, $\chi^2$, and SSE, the Elovich and pseudo-second-order models are more suitable than the pseudo-first-order models. The intra-particle diffusion was also well fitted to the Cr(VI) adsorption kinetics on Fe@FWB-OPT when the steps were divided at a turning point of 2 h.

3.4. Effect of reaction time

The results of the reaction time and fitted data using the kinetic models are shown in Figure S5. Cr(VI) adsorption can be divided into two steps: the immediate first step within 2 h and the relatively slower second step from 2 h to 24 h. The adsorption capacities for each step were 27.51 ± 0.64 and 49.76 ± 1.40 mg/g. The data from the reaction time were analyzed using pseudo-first-order, pseudo-second-order, Elovich, and intra-particle diffusion models (SI). Although the rate of adsorption reaction kinetics is not governed by first-or second-order reactions, pseudo-first-order and pseudo-second models are widely used to predict the adsorption kinetics (Simonin 2016). The Elovich model was derived from the assumption that adsorption proceeds on heterogeneous surfaces without desorption (Wu et al. 2009). Furthermore, the intra-particle diffusion model, which considers intra-particle diffusion as a rate-limiting step, was also employed (Weber &Morris 1963). The model fitted parameters and model accuracy indicators, including $R^2$, $\chi^2$, and the sum of squared errors (SSE), are listed in Tables S5 and S6. From $R^2$, $\chi^2$, and SSE, the Elovich and pseudo-second-order models are more suitable than the pseudo-first-order models. The intra-particle diffusion was also well fitted to the Cr(VI) adsorption kinetics on Fe@FWB-OPT when the steps were divided at a turning point of 2 h. With the appropriate description by pseudo-second-order and Elovich models, the adsorption rate at the initial stage was considered diffusion-limited. The overall adsorption rate is reduced by surface coverage and chemical adsorption (Simonin 2016, Wu et al. 2009). These results are also consistent with the results of the intra-particle diffusion model, in which the intercept of the regression equation of the first step was 0 mg/g and the regression lines passed through the origin, indicating that diffusion is a rate-limiting step for Cr(VI) adsorption (Pholosi et al. 2020).

3.5. Effect of temperature

The effects of the reaction temperature on Cr(VI) adsorption by Fe@FWB-OPT as a function of time are shown in Figure S6(a), and the Van't Hoff plot based on the thermodynamic model is shown in Figure S6(b). The thermodynamic parameters obtained from the Van't Hoff plot obtained by applying thermodynamic equations (provided in SI) are provided in Table S7. By increasing the temperature from 15°C to 35°C, the Cr(VI) adsorption capacity also increased from 33.09 ± 1.82 mg/g to 53.85 ± 0.57 mg/g. This result is consistent with the positive $\Delta H^0$, and which also indicates that the reaction in which Cr(VI) is adsorbed on Fe@FWB-OPT is an endothermic reaction. $\Delta S^0 > 0$ indicates that the disorder of the interfaces between the surface of Fe@FWB-OPT and the liquid phase was increased. In addition, $\Delta G^0$ values were 1.30–2.86 kJ/mol, which are relatively small and positive values, inferring that the Cr(VI) adsorption on Fe@FWB-OPT is a non-spontaneous reaction.

3.6. Effect of solution chemistry on Cr(VI) adsorption
As a factor for Cr(VI) removal by biochar, pH is a crucial factor in the Cr(VI) reduction reaction of biochar (Mandal et al. 2017). It is known that Cr(VI) can be adsorbed on the surface or reduced to Cr(III) at low pH with organic carbon according to the following equations (Liu et al. 2020, Mandal et al. 2017).

\[
\text{SurfaceR} + H^+ \rightarrow \text{SurfaceR}^+ \quad (6)
\]

\[
\text{SurfaceR}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{SurfaceR} - \text{Cr}_2\text{O}_7^{2-} \quad (7)
\]

\[
\text{Cr}_2\text{O}_7^{2-} + \text{organicC} + 10H^+ \rightarrow 2\text{Cr}^{3+} + \text{CO}_2 + 5\text{H}_2\text{O} \quad (8)
\]

As shown in Eq. (6-7), most previous studies on Cr(VI) removal using biochar presented the highest Cr(VI) removal at a low pH of 2 (Table 3). In this study, however, Cr(VI) adsorption capacity did not show a remarkable change depending on the pH, and it was maintained from pH 3 to 9 (36.27 ± 0.14 to 33.09 ± 0.14 mg/g). It did not drop sharply at pH 11 (27.64 ± 0.41 mg/g) (Figure 4). It can be inferred that Cr(VI) removal by Fe@FWB-OPT was achieved via mechanisms different from Eq. (7) and (8).

The Cr(VI) adsorption after reduction to Cr(III) by Fe(II), which was confirmed by XPS, is feasible regardless of the ionic species of Cr(VI). Therefore, it is considered as a major mechanism of Cr(VI) removal at various pH values (Ma et al. 2021, Yang et al. 2021).

When the pH was lower than pH 6.37, HCrO$_4^-$ is a major species, and CrO$_4^{2-}$ is a major species when the pH is greater than 6.37 (Figure 5(a)). Lu et al. (2017) presented the electrostatic attraction between HCrO$_4^-$ or CrO$_4^{2-}$ and Fe–OH$_2^+$ as one of the Cr(VI) adsorption mechanisms.

\[
\text{Fe} - \text{OH}_2^+ + \text{HCrO}_4^- \rightarrow \text{Fe} - \text{OH}_2^+ \cdots \text{HCrO}_4^- \quad (\cdots: \text{electrostaticattraction}) \quad (12)
\]

\[
\text{Fe} - \text{OH}_2^+ + \text{CrO}_4^{2-} \rightarrow \text{Fe} - \text{OH}_2^+ \cdots \text{CrO}_4^{2-} \quad (13)
\]

Furthermore, the XPS results indicated that Cr(VI) and Cr(III) were present in the adsorbed chromium. Therefore, it can be expected that there are other mechanisms for Cr(VI) removal by Fe@FWB-OPT.

The inhibitory effects of several oxyanions on Cr(VI) adsorption are shown in Figure S7. The Cr(VI) adsorption by Fe@FWB-OPT decreased by 90.5% (PO$_4^{3-}$), 85.2% (HCO$_3^-$), 26.5% (SO$_4^{2-}$), and 13.0% (NO$_3^-$) when the concentration of competing oxyanions was 10 mM. When PO$_4^{3-}$ was present, the Cr(VI) adsorption on Fe@FWB-OPT decreased the most, followed by HCO$_3^-$, SO$_4^{2-}$, and NO$_3^-$. The inhibitory effect of PO$_4^{3-}$ is considered to be the result of competitive adsorption of PO$_4^{3-}$, which has a tetrahedral structure similar to that of HCrO$_4^-$. (Lu et al. 2021, Lu et al. 2017).

### 4. Conclusions

The synthesis conditions for Fe-loaded food-waste biochar were investigated and optimized using RSM and ANN. RSM analysis confirmed that the pyrolysis temperature and Fe concentration are significant factors influencing the Cr(VI) adsorption capacity of Fe@FWB, while the pyrolysis time was not significant. ANN analysis showed the different significance of variables from the RSM analysis: pyrolysis temperature > pyrolysis time > Fe concentration. This difference between the RSM and ANN results can be explained by the fact that the significance was evaluated individually or in combination by RSM and evaluated as a whole by ANN. Fe@FWB, optimized using RSM with higher $R^2$ and lower SSE than ANN, was investigated for further study to explore its physical/chemical properties and Cr(VI) adsorption characteristics. The Langmuir and Redlich–Peterson models are better fitted models than the Freundlich model, indicating that the Cr(VI) adsorption of Fe@FWB-OPT was monolayer adsorption. The Cr(VI) sorption capacity of Fe@FWB-OPT was 377.71 mg/g, which is higher than that of other adsorbents, even though the result was obtained under neutral pH conditions. According to the description by pseudo-second-order and Elovich models, the Cr(VI) adsorption kinetics are limited by diffusion at a rapid initial adsorption rate, and the overall adsorption rate is reduced by the surface coverage. The adsorption of Cr(VI) onto Fe@FWB-OPT was not remarkably affected by the solution pH because the main mechanism of Cr(VI) adsorption is that the reduced Cr(III) is adsorbed to Fe$^{3+}$. The XPS analysis indicated that both Cr(III) and Cr(VI) were adsorbed on the surface of Fe@FWB-OPT, and Cr(VI) was adsorbed on the Fe@FWB-OPT via electrostatic interactions.

### Declarations
Funding

The authors received no specific funding for this study.

Authors' contributions

Jin-Kyu Kang: Formal analysis, Writing-original draft; Eun-Jin Seo: Experiment, Formal analysis, Data curation; Chang-Gu Lee: Conceptualization, Writing-reviewing and editing; Sanghyun Jeong: Writing-reviewing and editing; Seong-Jik Park: Conceptualization, Writing-original draft, Writing—Reviewing and Editing, Supervision

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Consent for participation: Not applicable

Availability of data and materials

All data generated or analysed during this study are included in this published article.

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Conflicts of interest

The authors declare no conflicts of interest.

References

1. Ali S, Noureen S, Shakoor MB, Haroon MY, Rizwan M, Jilani A, Arif MS, Khalil U (2020): Comparative evaluation of wheat straw and press mud biochars for Cr(VI) elimination from contaminated aqueous solution. Environ Technol Innov 19, 101017. https://doi.org/10.1016/j.eti.2020.101017
2. Belhachemi M, Addoun F (2011): Comparative adsorption isotherms and modeling of methylene blue onto activated carbons. Appl Water Sci 1, 111-117. 10.1007/s13201-011-0014-1
3. Bharagava RN, Mishra S (2018): Hexavalent chromium reduction potential of Cellulosimicrobium sp. isolated from common effluent treatment plant of tannery industries. Ecotoxicol Environ Saf 147, 102-109. https://doi.org/10.1016/j.ecosaf.2017.08.040
4. Cheng Q, Li C, Xu L, Li J, Zhai M (2011): Adsorption of Cr(VI) ions using the amphiphilic gels based on 2-(dimethylamino)ethyl methacrylate modified with 1-bromoalkanes. Chem Eng J 173, 42-48. https://doi.org/10.1016/j.cej.2011.07.033
5. Choudhary B, Paul D (2018): Isotherms, kinetics and thermodynamics of hexavalent chromium removal using biochar. J Environ Chem Eng 6, 2335-2343. https://doi.org/10.1016/j.jece.2018.03.028
6. Christensen JM (1995): Human exposure to toxic metals: factors influencing interpretation of biomonitoring results. Sci Total Environ 166, 89-135. 10.1016/0048-9697(95)04478-j
7. Coates J (2006): Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry. John Wiley & Sons
8. Ding J, Zhong Q, Zhang S, Cai W (2015): Size- and shape-controlled synthesis and catalytic performance of iron–aluminum mixed oxide nanoparticles for NOX and SO2 removal with hydrogen peroxide. J Hazard Mater 283, 633-642. https://doi.org/10.1016/j.jhazmat.2014.10.010
9. Dong H, Deng J, Xie Y, Zhang C, Jiang Z, Cheng Y, Hou K, Zeng G (2017): Stabilization of nanoscale zero-valent iron (nZVI) with modified biochar for Cr(VI) removal from aqueous solution. J Hazard Mater 332, 79-86. https://doi.org/10.1016/j.jhazmat.2017.03.002
10. Dong X, Ma LQ, Li Y (2011): Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. J Hazard Mater 190, 909-915. https://doi.org/10.1016/j.jhazmat.2011.04.008
11. Espinoza-Sánchez MA, Arévalo-Niño K, Quintero-Zapata I, Castro-González I, Almaguer-Cantú V (2019): Cr(VI) adsorption from aqueous solution by fungal bioremediation based using Rhizopus sp. J Environ Manag 251, 109595. https://doi.org/10.1016/j.jenvman.2019.109595
12. Hemmat Esfe M, Mahian O, Hajmohammad MH, Wongwises S (2018): Design of a heat exchanger working with organic nanouids using multi-objective particle swarm optimization algorithm and response surface method. Int J Heat Mass Transfer 119, 922-930. https://doi.org/10.1016/j.ijheatmasstransfer.2017.12.009
13. Herath A, Layne CA, Perez F, Hassan EIB, Pittman CU, Mlsna TE (2021): KOH-activated high surface area Douglas Fir biochar for adsorbing aqueous Cr(VI), Pb(II) and Cd(II). Chemosphere 269, 128409. https://doi.org/10.1016/j.chemosphere.2020.128409
14. Hong H, Jiang W-T, Zhang X, Tie L, Li Z (2008): Adsorption of Cr(VI) on STAC-modified rectorite. Appl Clay Sci 42, 292-299. https://doi.org/10.1016/j.claysci.2008.01.015
15. Hong S-H, Lyonga FN, Kang J-K, Seo E-J, Lee C-G, Jeong S, Hong S-G, Park S-J (2020): Synthesis of Fe-impregnated biochar from food waste for Selenium(0) removal from aqueous solution through adsorption: Process optimization and assessment. Chemosphere 252, 126475. https://doi.org/10.1016/j.chemosphere.2020.126475
16. Hu H, Sun L, Wang T, Lv C, Gao Y, Zhang Y-F, Wu H, Chen X (2019): Nano-ZnO functionalized biochar as a superhydrophobic biosorbent for selective recovery of low-concentration Re(VII) from strong acidic solutions. Miner Eng 142, 105885. https://doi.org/10.1016/j.mineng.2019.105885
17. Hu X, Ding Z, Zimmerman AR, Wang S, Gao B (2015): Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis. Water Res 68, 206-216. https://doi.org/10.1016/j.watres.2014.10.009

18. Huang L, Zhou S, Jin F, Huang J, Bao N (2014): Characterization and mechanism analysis of activated carbon fiber felt-stabilized nanoscale zero-valent iron for the removal of Cr(VI) from aqueous solution. Colloids Surf, A 447, 59-66. https://doi.org/10.1016/j.colsurfa.2014.01.037

19. Jang H-Y, Kang J-K, Park J-A, Lee S-C, Kim S-B (2020): Metal-organic framework MIL-100(Fe) for dye removal in aqueous solutions: Prediction by artificial neural network and response surface methodology modeling. Environ Pollut 267, 115583. https://doi.org/10.1016/j.envpol.2020.115583

20. Kang J-K, Seo E-J, Lee C-G, Park S-J (2021): Fe-loaded biochar obtained from food waste for enhanced phosphate adsorption and its adsorption mechanism study via spectroscopic and experimental approach. J Environ Chem Eng, 105751. https://doi.org/10.1016/j.jece.2021.105751

21. Karthik R, Meenakshi S (2015): Removal of Cr(VI) ions by adsorption onto sodium alginate-polyaniline nanofibers. Int J Biol Macromol 72, 711-717. https://doi.org/10.1016/j.ijbiomac.2014.09.023

22. Keegan GM, Learmonth ID, Case CP (2008): A systematic comparison of the actual, potential, and theoretical health effects of cobalt and chromium exposures from industry and surgical implants. Crit Rev Toxicol 38, 645-74. 10.1080/104084040701845534

23. Khalil U, Bilal Shakoor M, Ali S, Rizwan M, Nasser Alyemeni M, Wijaya L (2020): Adsorption-reduction performance of tea waste and rice husk biochars for Cr(VI) elimination from wastewater. J Saudi Chem Soc 24, 799-810. https://doi.org/10.1016/j.jscc.2020.07.001

24. Khayet M, Seman MNA, Hilal N (2010): Response surface modeling and optimization of composite nanofiltration modified membranes. J Membr Sci 349, 112-22. https://doi.org/10.1016/j.memsci.2009.11.031

25. Kim M-J, Hong S-H, Lee J-H, Lee C, Park S-J (2019): Removal of fluoride from water using thermally treated dolomite and optimization of experimental conditions using response surface methodology. Desalin Water Treat 155, 311-320.

26. Lee N, Hong S-H, Lee C-G, Park S-J, Lee J (2021): Conversion of cattle manure into functional material to remove selenate from wastewater. Chemosphere 278, 130398. https://doi.org/10.1016/j.chemosphere.2021.130398

27. Lee Y, Kim S, Kwon EE, Lee J (2020): Effect of carbon dioxide on thermal treatment of food waste as a sustainable disposal method. J CO2 Util 36, 76-81. https://doi.org/10.1016/j.jcou.2019.11.004

28. Lian Q, Wang B, Lee X, Li L, Liu T, Luu W (2019): Enhanced removal of hexavalent chromium by engineered biochar composite fabricated from phosphogypsum and distillers grains. Sci Total Environ 697, 134119. https://doi.org/10.1016/j.scitotenv.2019.134119

29. Liang J, Chen Y, Cai M, Gan M, Zhu J (2021): One-pot pyrolysis of metal-embedded biochar derived from invasive plant for efficient Cr(VI) removal. J Environ Chem Eng 9, 105714. https://doi.org/10.1016/j.jece.2021.105714

30. Lin X, Liu J, Wan S, He X, Cui L, Wu G (2019): A novel strategy for Cr(VI) removal from aqueous solution via CYP@IL101/chitosan capsule. Int J Biol Macromol 136, 35-47. https://doi.org/10.1016/j.ijbiomac.2019.05.125

31. Liu P, Ptsacek CJ, Blowes DW, Finfrock YZ, Liu Y (2020): Characterization of chromium species and distribution during Cr(VI) removal by biochar using confocal micro-X-ray fluorescence redox mapping and X-ray absorption spectroscopy. Environ Int 134, 105216. https://doi.org/10.1016/j.envint.2019.105216

32. Llorens E, Ibañez H, del Valle LJ, Puiggalí J (2015): Biocompatibility and drug release behavior of scaffolds prepared by coaxial electrospinning of poly(butylene succinate) and polyethylene glycol. Mater Sci Eng, C 49, 472-484. https://doi.org/10.1016/j.msec.2015.01.039

33. Lu J, Xu K, Yang J, Hao Y, Cheng F (2017): Nano iron oxide impregnated in chitosan bead as a highly efficient sorbent for Cr(VI) removal from water. Carbohydr Polym 173, 28-36. https://doi.org/10.1016/j.carbpol.2017.05.070

34. Lu J, Li B, Li W, Zhang X, Zhang W, Zhang P, Su R, Liu D (2021): Nano iron oxides impregnated chitosan beads towards aqueous Cr(VI) elimination: Components optimization and performance evaluation. Colloids Surf, A 625, 126902. https://doi.org/10.1016/j.colsurfa.2021.126902

35. Lyonga FN, Hong S-H, Cho E-J, Kang J-K, Lee C-G, Park S-J (2020): As(III) adsorption onto Fe-impregnated food waste biochar: experimental investigation, modeling, and optimization using response surface methodology. Environ Geochem Health. 10.1007/s10653-020-00739-4

36. Ma R, Yan X, Pu X, Fu X, Bai L, Du Y, Cheng M, Qian J (2021): An exploratory study on the aqueous Cr(VI) removal by the sulfate reducing sludge-based biochar. Sep Purif Technol, 119314. https://doi.org/10.1016/j.seppur.2021.119314

37. Mandal S, Sarkar B, Bolan N, OkYS, Naidu R (2017): Enhancement of chromate reduction in soils by surface modified biochar. J Environ Manag 186, 277-284. https://doi.org/10.1016/j.jenvman.2016.05.034

38. Mei L, Qiao H, Ke F, Peng C, Hou R, Wan X, Cai H (2020): One-step synthesis of zirconium dioxide-biochar derived from Camellia oleifera seed shell with enhanced removal capacity for fluoride from water. Appl Surf Sci 509, 144685. https://doi.org/10.1016/j.apsusc.2019.144685

39. Meilani V, Lee J-I, Kang J-K, Lee C-G, Jeong S, Park S-J (2021): Application of aluminum-modified food waste biochar as adsorbent of fluoride in aqueous solutions and optimization of production using response surface methodology. Microporous Mesoporous Mater 312, 110764. https://doi.org/10.1016/j.micromeso.2020.110764

40. Mishra S, Bharagava RN (2016): Toxic and genotoxic effects of hexavalent chromium in environment and its bioremediation strategies. J Environ Sci Health C Environ Carcinog Ecotoxicol Rev 34, 1-32. 10.1080/10599050.2015.1096883

41. Mohan D, Rajput S, Singh VK, Steele PH, Pittman CU (2011): Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. J Hazard Mater 188, 319-333. https://doi.org/10.1016/j.jhazmat.2011.01.127

42. Mojet BL, Ebbesen SD, Lefferts L (2010): Light at the interface: the potential of attenuated total reflection infrared spectroscopy for understanding heterogeneous catalysis in water. Chem Soc Rev 39, 4643. 10.1039/c0cs00014k

43. Montgomery DC (2017): Design and analysis of experiments. John wiley & sons
44. Myers RH, Montgomery DC, Anderson-Cook CM (2016): Response Surface Methodology: Process and Product Optimization Using Designed Experiments. Wiley

45. Owall M, Aroua MK, Daud WAW, Baroutian S (2009): Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review. Water, Air, Soil Pollut 200, 59-77. 10.1007/s11270-008-9893-7

46. Park S-J, An HK (2016): Optimization of fabrication parameters for nanofibrous composite membrane using response surface methodology. Desalin Water Treat 57, 20188-20198. 10.1080/19443994.2015.1109557

47. Plohoski A, Naidoo EB, Ofomaja AE (2020): Intraparticle diffusion of Cr(VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study. S Afr J Chem Eng 32, 39-55. https://doi.org/10.1016/j.sajce.2020.01.005

48. Puziy AM, Poddubnaya OI, Socha RF, Gurgul J, Wisniewski M (2008): XPS and NMR studies of phosphoric acid activated carbons. Carbon 46, 2113-2123. https://doi.org/10.1016/j.carbon.2008.09.010

49. Reguyal F, Sarmah AK (2018): Adsorption of sulfamethoxazole by magnetic biochar: Effects of pH, ionic strength, natural organic matter and 17α-ethinylestradiol. Sci Total Environ 628-629, 722-730. 10.1016/j.scitotenv.2018.01.323

50. Rowbotham AL, Levy LS, Shuker FK (2000): Chromium in the environment: an evaluation of exposure of the UK general population and possible adverse health effects. J Toxicol Environ Health B Crit Rev 3, 145-78. 10.1080/10937400050045255

51. Shaka K, Agarwal T (2019): Removal of Cr(VI) from water using pineapple peel derived biochars: Adsorption potential and re-usability assessment. J Mol Liq 293, 111497. https://doi.org/10.1016/j.molliq.2019.111497

52. Simonin J-P (2016): On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics. Chem Eng J 300, 254-263. https://doi.org/10.1016/j.cej.2016.04.079

53. Simons WW (1978): The Sadler handbook of infrared spectra. Sadler Research Laboratories, Philadelphia

54. Srivastava S, Agrawal SB, Mondal MK (2015): Biosorption isotherms and kinetics of removal of Cr(VI) using native and chemically modified Lagerstroemia speciosa bark. Ecol Eng 85, 56-66. https://doi.org/10.1016/j.ecoleng.2015.10.011

55. Swenson H, Stadie NP (2019): Langmuir's Theory of Adsorption: A Centennial Review. Langmuir 35, 5409-5426. 10.1021/acs.langmuir.9b00154

56. Tan X-F, Liu Y-G, Gu Y-I, Xu Y, Zeng G-M, Hu X-J, Liu S-B, Wang X, Liu S-M, Li J (2016): Biochar-based nano-composites for the decontamination of wastewater: A review. Bioresour Technol 212, 318-333. https://doi.org/10.1016/j.biortech.2016.04.093

57. Terzyk AP (2001): The influence of activated carbon surface chemical composition on the adsorption of acetaminophen (paracetamol) in vitro: Part II. TG, FTIR, and XPS analysis of carbons and the temperature dependence of adsorption kinetics at the neutral pH. Colloids Surf, A 177, 23-45. https://doi.org/10.1016/S0927-7757(00)00594-X

58. Turan NG, Meseci B, Ozgonenel O (2011): The use of artificial neural networks (ANN) for modeling of adsorption of Cu(II) from industrial leachate by pumice. Chem Eng J 171, 1091-1097. https://doi.org/10.1016/j.cej.2011.05.005

59. Weber WJ, Morris JC (1963): Kinetics of Adsorption on Carbon from Solution. Journal of the Sanitary Engineering Division 89, 31-59. doi:10.1061/JSEDAI.0000430

60. Wei D, Li B, Huang H, Luo L, Zhang J, Yang Y, Guo J, Tang L, Zeng G, Zhou Y (2018): Biochar-based functional materials in the purification of agricultural wastewater: Fabrication, application and future research needs. Chemosphere 197, 165-180. https://doi.org/10.1016/j.chemosphere.2017.12.193

61. World Health O (2017): Guidelines for drinking-water quality: fourth edition incorporating first addendum. World Health Organization, Geneva

62. Wu F-C, Tseng R-L, Juang R-S (2009): Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. Chem Eng J 150, 366-373. https://doi.org/10.1016/j.cej.2009.01.014

63. Wu F-C, Liu B-L, Wu K-T, Tseng R-L (2010): A new linear form analysis of Redlich–Peterson isotherm equation for the adsorptions of dyes. Chem Eng J 162, 21-27. https://doi.org/10.1016/j.cej.2010.03.006

64. Yang X, Hu L, Bai J, Mao X, Chen X, Wang X, Wang S (2021): Increased structural defects of graphene oxide compromised reductive capacity of ZVI towards hexavalent chromium. Chemosphere 277, 103928. 10.1016/j.chemosphere.2021.130308

65. Yetilmezsoy K, Demirel A (2008): Artificial neural network (ANN) approach for modeling of Pb(II) adsorption from aqueous solution by Antep pistachio (Pistacia vera L.) shells. J Hazard Mater 153, 1288-300. https://doi.org/10.1016/j.ijhazmat.2007.09.092

66. Yoshinaga M, Ninomiya H, Al Hossain MMA, Sudo M, Ahssan N, Alim MA, Khalequzzaman M, Iida M, Yajima I, Ohgami N, Kato M (2018): A comprehensive study including monitoring, assessment of health effects and development of a remediation method for chromium pollution. Chemosphere 201, 667-675. 10.1016/j.chemosphere.2018.03.026

67. Zhang W, Mao S, Chen H, Huang L, Qiu R (2013): Pb(II) and Cr(VI) sorption by biochars pyrolyzed from the municipal wastewater sludge under different heating conditions. Bioresour Technol 147, 545-552. https://doi.org/10.1016/j.biortech.2013.08.082

68. Zhang Y, Pan B (2014): Modeling batch and column phosphate removal by hydrated ferric oxide-based nanocomposite using response surface methodology and artificial neural network. Chem Eng J 249, 111-120. https://doi.org/10.1016/j.cej.2014.03.073

69. Zhao C, Hu L, Zhang C, Wang S, Wang X, Huo Z (2021): Preparation of biochar-interpenetrated iron-alginate hydrogel as a pH-independent sorbent for removal of Cr(VI) and Pb(II). Environ Pollut 287, 117303. https://doi.org/10.1016/j.envpol.2021.117303

70. Zhou L, Liu Y, Liu S, Yin Y, Zeng G, Tan X, Hu X, Hu X, Jiang L, Ding Y, Liu S, Huang X (2016): Investigation of the adsorption-reduction mechanisms of hexavalent chromium by ramie biochars of different pyrolytic temperatures. Bioresour Technol 218, 351-359. https://doi.org/10.1016/j.biortech.2016.06.102
Figure 1
Comparison of Cr(VI) adsorption capacity of Fe@FWB between the observed values and model predicted values by response surface methodology (RSM) and artificial neural network (ANN).

| Model  | R²       | SSE    |
|--------|----------|--------|
| RSM    | 0.9997   | 0.8745 |
| ANN    | 0.9997   | 0.8889 |

Figure 2
Estimated RSM (left side: (a), (c), and (e)) and ANN (right side: (b), (d), and (f)) for the adsorbed Cr(VI) to Fe@FWB. (a, b) Effects of temperature and Fe concentration when coded pyrolysis time = 0. (c, d) Effects of pyrolysis time and Fe concentration when coded pyrolysis temperature = 0. (e, f) Effects of pyrolysis time and pyrolysis temperature with coded Fe concentration. The units for X-axis are dimensionless because it is a coded value.
Figure 3

XPS spectra of Fe@FWB-OPT and Cr(VI) adsorbed Fe@FWB-OPT (Cr-Fe@FWB-OPT). (a) C1s of Fe@FWB-OPT, (b) C1s of Cr-Fe@FWB-OPT, (c) O1s of Fe@FWB-OPT, (d) O1s of Cr-Fe@FWB-OPT, (e) Fe2p of Fe@FWB-OPT, (f) Fe2p of Cr-Fe@FWB-OPT, (g) Cr2p of Fe@FWB-OPT, and (h) Cr2p of Cr-Fe@FWB-OPT.
Figure 4
Cr(VI) adsorption amount to Fe@FWB-OPT and final pH of solution regarding initial solution pH

Figure 5
Effect of pH on the ion species distribution using Visual MINTEQ 3.1 software: (a) Cr(VI) (500 mg/L), (b) Fe(II) (0.01 M), and (c) Fe(III) (0.01 M)

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- ESPRCrANNRSMSIV2.docx