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

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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 statically 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 selenite, 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, Meilani 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 FeCl₃ solution with 100 g of dried FW for 24 h. The mixture of FeCl₃ 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 N₂ 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):

$$Y = a_0 + \sum_{i=1}^3 a_i X_i + \sum_{i=1}^3 \sum_{j=1}^3 a_{i,j} X_i X_j + \sum_{i=1}^3 \sum_{j=1}^3 \sum_{k=1}^3 a_{i,j,k} X_i X_j X_k \quad (1)$$

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 $i = 1, 2$, and 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 composited 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:

$$\text{tansig}(x) = \frac{2}{1 + e^{-2x}} - 1 \quad (2)$$

$$\text{purelin}(x) = x \quad (3)$$

$$\begin{aligned} \begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,j} \end{bmatrix} &= \text{tansig} \left(\begin{bmatrix} w_{1,1} \\ \vdots \\ w_{1,j} \end{bmatrix} \times \begin{bmatrix} X_1 \\ X_2 \\ X_3 \end{bmatrix} + \begin{bmatrix} b_{1,1} \\ \vdots \\ b_{1,j} \end{bmatrix} \right) \\ Y &= \text{purelin} \left(w_{2,1} \times \begin{bmatrix} h_{1,1} \\ \vdots \\ h_{1,j} \end{bmatrix} + b_{2,1} \right) \end{aligned} \quad (4)$$

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 ($\bar{w}$) and bias set ($\bar{b}$) for the ANN optimization. However, the data included in the validation set varied with topology. Therefore, the best topology and its $\bar{w}$ and $\bar{b}$ 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 N₂ 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 α radiation (h ν = 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 Na₂HPO₄, 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:

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

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 (*R*²) and adjusted *R*² (*R*²_{adj}) were 0.9997 and 0.9989, respectively, indicating the high suitability of the RSM prediction. The *p*-values of *X*₂ and *X*₃ were less than 0.05 (<0.0001), while the *p*-value of *X*₁ 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 *X*₁ (*X*₁*X*₂, *X*₁², *X*₁²*X*₂, *X*₁²*X*₃, and *X*₁*X*₂²) exhibited relatively low *p*-values (< 0.05), except for the *X*₁*X*₃ term. Therefore, the pyrolysis time may also be significant when its effects are combined with other variables. The coefficient of *X*₂, 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 *X*₃, the terms containing *X*₃ 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	FValue	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
$X_1X_2^2$	28.05	1	28.05	128.30	0.0003
Residual	0.87	4	0.22		
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 $\bar{w}$ and $\bar{b}$ for topology 3:11:1 are presented in Table 2.

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

n	$w_{i,n}$			$b_{1,n}$	$w_{2,n}^T$	$b_{2,n}$
	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:

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

where E_i is the effect of each variable on the output (%). $i = 1, 2$, and 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_1) > 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 cm³/g accumulative volume, and the accumulative pore volume also increased to 0.0103 cm³/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 only 4.144 m²/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 CH₂ 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 Fe²⁺, Fe³⁺, 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 Fe²⁺ decreased, while the peak of Fe³⁺ 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 Fe²⁺ 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 $a_R C_e^g$ 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 , χ^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.

Table 3
Comparison of Cr(VI) adsorption capacities of Fe@FWB-OPT to other biochar adsorbents in literature

Adsorbent	Biochar origin	Adsorption capacity (mg/g)	pH	Size (mm)	Temp. (°C)	Ref.
Oak wood biochar	Oak wood	4.1	2	0.25 – 0.60	35	(Mohan et al. 2011)
Oak bark biochar	Oak bark	7.4	2	0.25 – 0.60	35	(Mohan et al. 2011)
Nanoscale zero-valent iron coated biochar	Cornstalk	17.8	5	unmentioned	25	(Dong et al. 2017)
Eucalyptus globulus bark biochar	Eucalyptus globulus bark	25.4	2	< 0.250	35	(Choudhary &Paul 2018)
Douglas fir biochar	byproduct of bio-syn gas production	32.5	2	0.1 - 0.5	35	(Herath et al. 2021)
Pineapple peel biochar	Pineapple peel	41.7	2	< 1	30	(Shakya &Agarwal 2019)
Fe-embedded biochar	Eichhornia crassipes	47.7	2	< 0.075	30	(Liang et al. 2021)
Distillers grain biochar	Distillers grain	63.1	3	unmentioned	22	(Lian et al. 2019)
Ramie biochar	Ramie	82.2	2	< 0.147	25	(Zhou et al. 2016)
KOH-activated Douglas fir biochar	byproduct of bio-syn gas production	120.1	2	0.1 - 0.5	35	(Herath et al. 2021)
Phosphogypsum + Distillers grain biochar	Phosphogypsum + Distillers grain	157.9	3	unmentioned	22	(Lian et al. 2019)
Press mud biochar	Press mud	190	5.2	unmentioned	20	(Ali et al. 2020)
Sludge biochar	Municipal wastewater sludge	208	2	< 0.250	25	(Zhang et al. 2013)
Wheat straw biochar	Wheat straw	215	5.2	unmentioned	20	(Ali et al. 2020)
Rick husk biochar	Rice husk	365.9	5.2	< 0.250	20	(Khalil et al. 2020)
Fe@FWB-OPT	Food waste	377.71	7.0	0.425	25.0	This study
Tea waste biochar	Tea waste	385.7	5.2	< 0.250	20	(Khalil et al. 2020)

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 sorption 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 , χ^2 , and the sum of squared errors (SSE), are listed in Tables S5 and S6. From R^2 , χ^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 ΔH^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, ΔG^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).

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).

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.

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.

However, $Fe-OH_2^+$ was the only dominant hydrolysis species of Fe(III) between pH 4.5 and 8.5 (Figure 5(c)). Therefore, it is necessary to consider all the Fe(II) hydrolysis and Fe(III) hydrolysis species. Both $HCrO_4^-$ and CrO_4^{2-} can also be adsorbed on the Fe^{2+} or positive Fe(II) hydrolysis species ($Fe_x(OH)_y^{2x-y}$, $2x-y>0$) and Fe^{3+} or the positive Fe(III) hydrolysis species ($Fe_x(OH)_y^{3x-y}$, $3x-y>0$) by electrostatic attraction. The above-mentioned positive Fe(II) and Fe(III) hydrolysis species were dominant below pH 10.8 and 8.5, respectively (when the concentration of Fe(II) or Fe(III) = 0.01 M) (Figure 5(b) and (c)). When the pH was greater than these values, $Fe(OH)_3^-$ and $Fe(OH)_4^-$ were dominant for Fe(II) and Fe(III) species. Therefore, the ion species change of Fe(II) or Fe(III) indicated that the Cr(VI) adsorption on Fe@FWB-OPT by electrostatic attraction was reduced at high pH, leading to the reduction of Cr(VI) adsorption by the increase in pH.

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^{2+} . 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

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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

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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.

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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)

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)

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