


Production and optimisation of adsorbent materials from teawaste for heavy metal removal from aqueous solution: feasibility of hexavalent chromium removal – kinetics, thermodynamics and isotherm study

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ABSTRACT

A face-centred central composite experimental design scheme was used to find experimental conditions this would result in producing magnetic bleached teawaste (MBTW) adsorbent material to have the optimum hexavalent chromium (Cr(VI)) removal capacity. The effect of treatment conditions, namely temperature (200 °C, 350 °C, 500 °C), duration of the heat treatment (2 h, 3 h, 4 h), the concentration of the iron chloride (0.02 g/g, 0.055 g/g, 0.09 g/g) added was investigated. The results obtained showed that the pyrolysis temperature and the amount of iron chloride added during treatment had significant effects on the performance of MBTW material in removal of both total chromium and Cr(VI). Increasing temperature from 200 °C to 500 °C, both Cr(VI) and total Cr removal would decrease. The material with optimum removal of Cr(VI) was used for the detailed adsorption study. The results from the detailed adsorption study indicated that the MBTW material has an excellent Langmuir removal capacity of Cr(VI) (269.9 mg/g). The Cr(VI) removal process also involved the reduction of the Cr(VI) to Cr(III). The removal process was shown to be temperature-dependent and endothermic. According to the FTIR analysis and the kinetic modelling results, chemisorption is the main mechanism responsible for the removal of the Cr(VI). The effect of background ions on the reduction of Cr(VI) was also investigated and the results show that presence of carbonate ions caused a huge reduction in removal of Cr(VI) while chloride ions had the least effect.

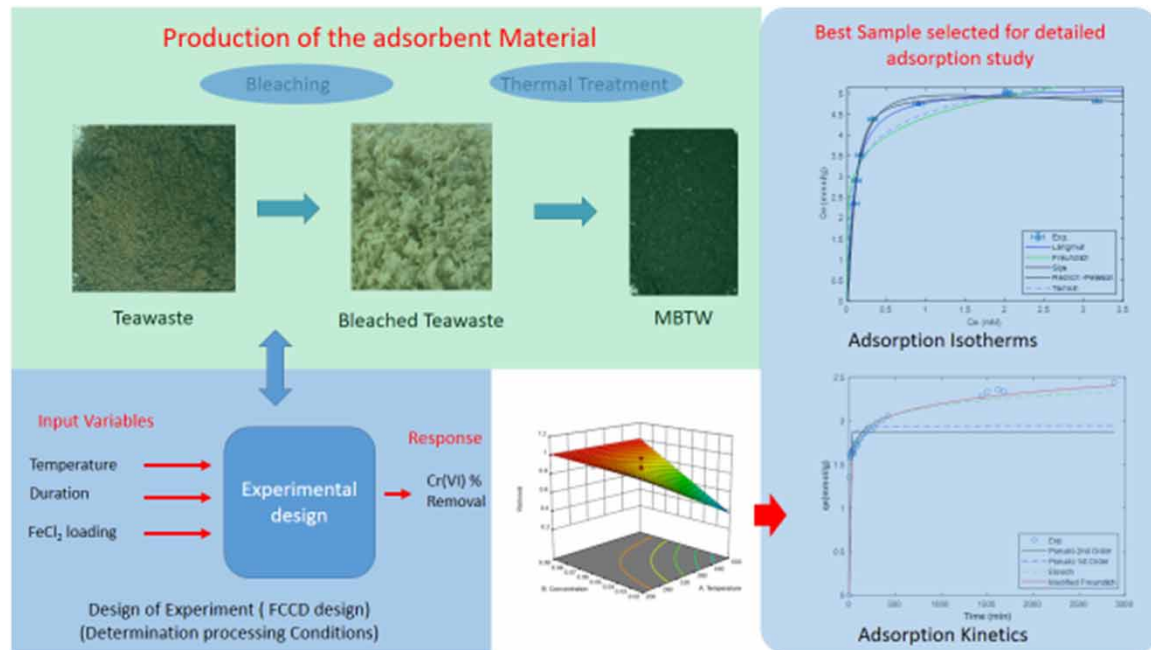
Key words: adsorption, biomass, chromium, experimental design, reduction, teawaste

HIGHLIGHTS

- Magnetic adsorbent material was successfully produced from teawaste. This makes it easier to separate the adsorbent from solution after the adsorption process.
- Optimum iron nanoparticles loading and pyrolysis temperature was determined.
- Magnetic adsorbent material produced has high removal capacity towards hexavalent Cr (~270 mg/g).
- Hexavalent removal process was found to be endothermic.

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GRAPHICAL ABSTRACT



1. INTRODUCTION

Effective treatment of heavy metal wastewater is presently a severe challenge worldwide, as a result of the rapid development of industry in recent years. Toxic heavy metals such as cadmium, lead, nickel, zinc and chromium are the major hazardous pollutants in the wastewater, which can cause great damage to water environment quality and then further do harm to human beings through the food chain (Salem *et al.* 2000; Tchounwou *et al.* 2012; Burakov *et al.* 2018). Among these heavy metals, chromium is known as one of the most hazardous heavy metals released by pigment, electroplating, tanning and other industries (Owlad *et al.* 2009; Dehghani *et al.* 2016; Jin *et al.* 2016). The toxicity of chromium is related to its existing valence state. Compared to Cr with other valence states, Cr(VI) is the most toxic and prolonged exposure to Cr(VI) can seriously cause gastrointestinal diseases, vomiting, abdominal pain, dyspnoea and even genetic mutations (Owlad *et al.* 2009; Pereira *et al.* 2012; Gupta & Balomajumder 2015; Dehghani *et al.* 2016; Jin *et al.* 2016). Therefore, the removal of Cr(VI) from wastewater is crucial before it can be discharged into the external water environment.

So far, multiple studies have revealed enhanced technologies for Cr(VI) removal from wastewater, including ion exchange (Galán *et al.* 2005; Li *et al.* 2017), membrane separation (Ho & Poddar 2001; Yang *et al.* 2014), chemical precipitation (Mirbagheri & Hosseini 2005), ultrafiltration (Ghosh & Bhattacharya 2006), electrocoagulation (Gao *et al.* 2005) and biosorption. Among all these technologies, biosorption is recognised as an effective method for heavy metal removal for wastewater treatment. The biosorption process is more flexible in both design and operation parts, also the adsorbents, usually with a lower price, can be regenerated and reused after appropriate desorption processes. According to recent studies, various materials, such as treated waste newspaper (Dehghani *et al.* 2016); fruit shell (Anandkumar & Mandal 2009); rice straw (Wu *et al.* 2016); modified seaweed (Yang & Chen 2008); teawaste (Gupta & Balomajumder 2015); sawdust (Meghna & Mondal 2013); bio-waste granules (Jaiyeola *et al.* 2020), banana peel (Chen *et al.* 2022) and so on, have all been examined as biosorbents for Cr(VI) removal from wastewater.

It was reported that about 170 million cups of tea would be consumed daily in the UK alone (Mangwandi *et al.* 2014). The excessive consumption of tea would cause enormous quantities of teawaste, which is discarded into the environment. No treatment is required if the teawaste is to be disposed off through composting. Therefore, dealing with these tea wastes is critical for suitable development of the UK. Recently, using teawaste as a bio-adsorbent for Cr(VI) removal is attracting widespread attention. In another study, green-teawaste leaves were utilised as adsorbents for the removal of Cr(VI); removal efficiency of Cr(VI) could be achieved up to 99% and the maximum removal capacity was 34.59 mg/g were reported (Jeyaseelan & Gupta 2016). Albadarin *et al.* also

investigated pure teawaste as an adsorbent for Cr(VI) removal, the study revealed that biosorption capacity was up to 107.8 mg/g (Albadarin *et al.* 2013). Though many researchers have reported that the original teawaste has a good removal capacity of heavy metals and other pollutants in aqueous solutions (Albadarin *et al.* 2013; Gupta & Balomajumder 2015; Thapak *et al.* 2015; Jeyaseelan & Gupta 2016). However, it is well recognized that the original teawaste can go mouldy with considerable ease. This would cause a challenge for further using this kind of waste in the wastewater treatment area. Therefore, how to treat the teawaste for further utilisation is crucial for using the teawaste as bio-adsorbents.

Thapak *et al.* used chemically activated (acid) teawastes as adsorbents for the Cr(VI) removal, they found that the maximum removal percentage of the Cr(VI) was nearly 94% at its optimum conditions (Thapak *et al.* 2015). In addition, magnetic teawaste was reported to have a superior capacity for Cr(VI) adsorption by Wen *et al.* (21.23 mg/g) and Fan *et al.* (75.76 mg/g) (Fan *et al.* 2017; Wen *et al.* 2017). During these years, magnetic carbon adsorbents have demonstrated advantages in the removal of environmental pollutants including heavy metal ions and organic compounds due to their easy separation after the adsorption process. Among all these studies, there are few reports of using magnetic bleached teawaste (MBTW) as an adsorbent for Cr(VI) removal. As the bleached teawaste reported by Saygılı *et al.* could increase the adsorption capacity of the methylene blue (Saygılı *et al.* 2018). Our previous study showed that MBTW had a relatively high removal capacity for Cr(VI) compared to bleached teawaste and magnetic teawaste (Jiahong 2021). Therefore, the primary objective of this investigation was to (1) optimise the process variables of MBTW production for Cr(VI) removal; (2) characterise the MBTW; and (3) explore the adsorption performance of such teawaste on the removal of Cr(VI) from aqueous solutions.

2. MATERIALS AND METHODS

2.1. Chemicals

The chemicals used in this study were analytical grade obtained from Sigma Aldrich (UK): potassium dichromate, 1,5-diphenylcarbohydrazide, nitric acid, sulphuric acid, methanol, and iron (III) chloride hexahydrate.

2.2. Production of MBTW

Teawaste, collected from the local coffee shop, was thoroughly washed several times with hot water to remove any colour and soluble components. It was then dried in an oven at 65 °C for 24 hours. The materials obtained after drying (DTW) were modified by household bleach (containing 6% NaOCl) to improve the surface oxygen groups and active sites of the original teawaste. The modification method was based on the technique reported by Saygılı *et al.* (2018). The DTW was modified by adding bleach, and an electric stirrer was used to stir the mixture for 10 hours after the bleach was added. The mixture was then rinsed with distilled water. This cycle was repeated two or three times until the colour of the mixture totally changed from black to white and then the mixture was filtered and dried at 60 °C for 24 hours. The dried mixture was named bleached teawaste.

A central composite experimental design was used to optimise the process variables of MBTW production for Cr(VI) removal for the next stage. Based on our previous study, each of the three varieties was varied at three different levels: low (−1), middle (0) and high (+1). The pyrolysis temperature (A) used was varied at 200 °C, 350 °C and 500 °C; for the concentration of FeCl₃ solution (B), the levels were 0.02 g/g, 0.055 g/g and 0.09 g/g; the levels of pyrolysis time C were 2, 3 and 4 h. The details of the experiments are shown in Table 1.

According to conditions shown in Table 1, 300 mL FeCl₃ solution with predetermined concentration was used for each 30 g bleached teawaste residue. The mixture was filtered and dried at 60 °C for 24 hours after being stirred for 4 hours and kept overnight. In the end, the dried FeCl₃ treated bleach teawaste was heated under oxygen-limited conditions in a muffle furnace. The product obtained was called MBTW.

2.3. Characterisation of MBTW

Elemental analysis data was obtained using a Perkin Elmer PE2400 CHNS Elemental Analyzer. For the SEM analysis, the MBTW samples were coated with gold and vacuumed for electron reflection before analysis on JOEL_JSM 6400 scanning microscope. A Fourier transform infrared (FT-TR) spectrophotometer (PerkinElmer Spectrum I) was applied to measure the functional groups of the MBTW samples by using the KBr pellet method at the scanning ranges of 4,000–400 cm^{−1}.

Table 1 | Experimental design of MBTW production for Cr removal

Run	A: Temperature °C	B: Concentration g/g	C: Time h	Cr(VI) Removal %	Total Cr Removal %
1	500	0.09	2	97.0	57.7
2	500	0.02	2	34.3	30.8
3	350	0.055	3	87.3	57.6
4	500	0.09	4	99.4	57.6
5	200	0.09	4	98.1	57.7
6	500	0.02	4	31.1	30.2
7	200	0.02	2	94.6	60.8
8	350	0.055	4	97.0	56.4
9	200	0.09	2	98.1	57.4
10	500	0.055	3	93.3	55.7
11	350	0.055	3	97.2	55.8
12 ^a	200	0.055	3	98.2	57.9
13	350	0.09	3	97.4	58.4
14	350	0.02	3	43.3	40.8
15	350	0.055	3	97.3	59.7
16	350	0.055	2	94.9	61.0
17	200	0.02	4	88.0	63.7

^aBest sample highlighted.

2.4. Adsorption studies

Metal solutions were prepared from a stock synthetic wastewater solution of 1,000 ppm (mg/L) Cr(VI), using potassium dichromate dissolved in deionised water. Based on the previous studies, the best working pH value was 2 for the Cr(VI) adsorption. Therefore, all studies carried out in this research were conducted at a pH of 2 using nitric acid (Albadarin *et al.* 2014, 2017). The colour development reagent used for the determination of Cr(VI) concentration was prepared using the method described by Albadarin *et al.* (2013). In this method, the reagent would react with Cr(VI) to form a purple-red complex in an acid solution. Then, the concentration of Cr(VI) was determined at the wavelength of 540 nm by UV-VIS spectrophotometer (Perkin Elmer Lambda 800, PerkinElmer Inc. USA) using the absorbance of deionised water as the reference. In addition, the concentration of total Cr after the adsorption process was determined using atomic absorption spectroscopy (AAS) (Perkin Elmer Analyst 100, PerkinElmer Inc. USA). The determination of Cr(III) was obtained from the difference between total Cr and Cr(VI). The Cr(VI) and total Cr removal reflect the decrease of Cr(VI) after adsorption and the reduction of the Cr(VI) concentration due to the generation of Cr(III) for the oxidation process and their adsorption respectively. The removal percentage R was calculated as below:

$$R = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\% \quad (1)$$

where R (%) is the removal percentage; C_0 is the initial Cr(VI) concentration; C_t is the concentration of Cr(VI) or total Cr in the solution after adsorption.

All the experimental treatments were performed in duplicate with the average values reported. Additional analyses were conducted whenever two measurements showed a difference larger than 5%. The concentration of Cr(VI) in the solid phase is given by the following formula:

$$q_t = \frac{(C_i - C_t)}{m} \times V \quad (2)$$

q_t (mg/g) is the amount of Cr(VI) adsorbed to the solid phase at time t (min), C_i is the initial Cr(VI) concentration, C_t (mg/L) is the concentration of Cr(VI) at time t , V (L) is the volume of Cr(VI) solution and the mass of the biosorbent in gram is m .

2.5. Selection of the best MBTW for Cr(VI) removal

MBTW produced under predetermined conditions was used to evaluate the effect of different MBTW on Cr(VI) removal. At a fixed dosage of 5 g/L, 0.1 g MBTW was added to glass vials (60 mL) containing 20 mL chromium solutions with the initial concentration of 300 ppm (pH = 2). After being placed on a shaker (Gerhardt) at 150 rpm at room temperature for 24 h, samples were taken for concentration analysis.

2.6. Detailed adsorption with the best MBTW sample

After selection of the best sample from the 17 samples of MBTW produced (as per section 2.4), a detailed adsorption study was conducted to obtain the optimum dosage, adsorption capacity and study kinetics as described in the subsection below:

2.6.1. Effect of dosage

To investigate the effect of the adsorbent dosage on the removal of the Cr(VI) different amounts of the MBTW (0.5 g/L, 2.5 g/L, 3.5 g/L, 5 g/L and 7.5 g/L) were added to glass vials containing 20 mL chromium solutions with an initial concentration of 300 ppm (pH = 2). After being placed on a shaker (Gerhardt) at 150 rpm at room temperature for 24 h, samples were taken for concentration analysis.

2.6.2. Effect of concentration at different temperature

The adsorption isotherm of Cr(VI) onto MBTW was investigated by adding 0.05 g of MBTW adsorbent into each glass vial containing 20 mL chromium solutions with initial concentrations ranging from 250 to 800 ppm. The 7 glass vials with different chromium concentrations were placed in a water-baths with a pre-set temperature (room temperature, 30 °C, 40 °C, 50 °C and 60 °C). The temperature was controlled by a magnetic hotplate stirrer (Radleys) under the bath. The magnetic stir was set at 500 rpm during the adsorption experiment. The samples were extracted for concentration analysis after 48 h.

2.6.3. The kinetic study

The kinetics of the MBTW for the Cr(VI) removal was investigated using a fixed dosage of the biosorbent. The MBTW adsorbent was carefully weighed and added to a 300 mL chromium solution with an initial concentration of 300 ppm (pH = 2) to obtain a dose of 2.5 g/L. The beaker was then placed on the hotplate (Radleys) at room temperatures with a magnetic stirring speed of 200 rpm for 48 hours. Samples were collected (0.1 mL) at different time intervals for concentration analysis.

2.6.4. Effect of background ions

Different salts were added to chromium solution with concentration of 100 ppm to study the effect of the presence of others ions on the removal of chromium (VI). The conditions of the experiments were as follows: salt: 0.1 mol/l NaCl, NH₄Cl, K₂SO₄, NaNO₃, NaHCO₃ and blank; solution pH 2; initial Cr(VI) concentrations 100 ppm; shaking time 3 days at 110 rpm; MBTW dose 2.5 g/L; room temperature.

3. RESULTS AND DISCUSSION

3.1. Optimisation of treatment variables of MBTW production for Cr removal

During the Cr removal experiments, it was found that all the MBTW samples produced could be efficiently separated from an aqueous solution by using a permanent magnet. The results of Cr(VI) removal and total Cr removal of MBTW produced under different process conditions are shown in Table 1. As can be seen from the table, the maximum Cr(VI) removal percentage was around 99%; however, the maximum total Cr removal percentage was around 64%. In addition, it was observed that the total Cr removal was less than the Cr(VI) removal when the same MBTW was used, which indicated that a portion of Cr(VI) was reduced to Cr(III) during the adsorption process. Many researchers have reported that there might be a reduction of some toxic Cr(VI) to non-toxic Cr(III) in the Cr removal process (Xu *et al.* 2015; Tian *et al.* 2016). To understand the influence of the treatment variables on the Cr removal, ANOVA analysis was performed using the Design-Expert software. Detailed ANOVA analysis results of the effect of treatment variables on the Cr(VI) removal and total

Cr removal are given in Table 2. For the removal of Cr(VI), the removal percentage could be expressed as coded variables:

$$R = 0.84 - 0.15A + 0.17B - 0.02C + 0.15AB \quad (3)$$

where A, B and C are the coded variables for pyrolysis temperature, the concentration of FeCl₃ solution and pyrolysis time, respectively.

Table 2 | ANOVA analysis table for Cr(VI) and total Cr removal

	Source	Sum of Squares	df	Mean Square	F-value	p-value
Cr(VI)	Model	0.6368	4	0.1592	23.5	<0.0001
	A	0.1919	1	0.1919	28.33	0.0005
	B	0.2715	1	0.2715	40.08	0.0001
	C	0.004	1	0.004	0.5839	0.4643
	AB	0.1741	1	0.1741	25.7	0.0007
	Residual	0.061	9	0.0068		
	Cor Total	0.6977	13			
	R ² = 0.9126					
total Cr	Model	0.1296	4	0.0324	28.17	<0.0001
	A	0.0502	1	0.0502	43.63	<0.0001
	B	0.027	1	0.027	23.46	0.0009
	C	0.0003	1	0.0003	0.2869	0.6052
	AB	0.0528	1	0.0528	45.92	<0.0001
	Residual	0.0104	9	0.0012		
	Cor Total	0.1399	13			
	R ² = 0.9260					

Judging from the *P*-value obtained in Table 2, the Interaction Model adequately described the dependence of Cr(VI) removal on the treatment variables since the *P*-value for the model was less than 0.0001. The most significant model terms were the concentration of FeCl₃ solution, pyrolysis temperature and the interaction of the two factors. However, it is interesting to see that the pyrolysis time was not included as a term in the equation, which indicated that changing the pyrolysis time did not have a significant effect on the Cr(VI) removal percentage.

The response surface plots showing the effect of process variables on MBTW production for Cr(VI) removal is illustrated in Figure 1(a). Compared with the high level of FeCl₃ concentration, the influence of temperature on the Cr(VI) removal was more significant when the low level of FeCl₃ concentration was used. When the temperature was increased from 200 °C to 500 °C, the Cr(VI) removal decreased from around 95% to less than 40%. This is in agreement with results reported by Wen *et al.*, which showed that the Cr(VI) adsorption capacities of the magnetic porous carbonaceous materials made from tea leaves decreased (from 21.23 mg/g to 12.33 mg/g) with the increasing pyrolysis temperature from 300 °C to 500 °C (Wen *et al.* 2017). According to Wen *et al.*, it was due to the relatively lower density of adsorptive sites on the γ -Fe₂O₃. It has also been reported that magnetic nanoparticles obtained at higher temperatures have a relatively higher crystallization degree and larger particle diameter and are more closely in contact with the porous carbon layer (Wu *et al.* 2012).

In addition, it was also observed that the FeCl₃ concentration could affect the Cr(VI) removal more significantly at the high pyrolysis temperature than that at the low pyrolysis temperature. For example, as shown in Figure 1(a), the Cr(VI) removal increased from around 35% to around 99% with the increasing FeCl₃ concentration in high pyrolysis temperature 500 °C. However, there was nearly no change in Cr(VI) removal when FeCl₃ concentration increased from 0.02 g/g to 0.09 g/g in the low pyrolysis temperature of 200 °C.

For the total Cr removal, the removal percentage could be expressed as coded variables as below:

$$R = 0.54 - 0.08A + 0.06B + 0.01C + 0.08AB \quad (4)$$

where A, B and C are the coded variables for pyrolysis temperature, the concentration of FeCl₃ solution and pyrolysis time, respectively.

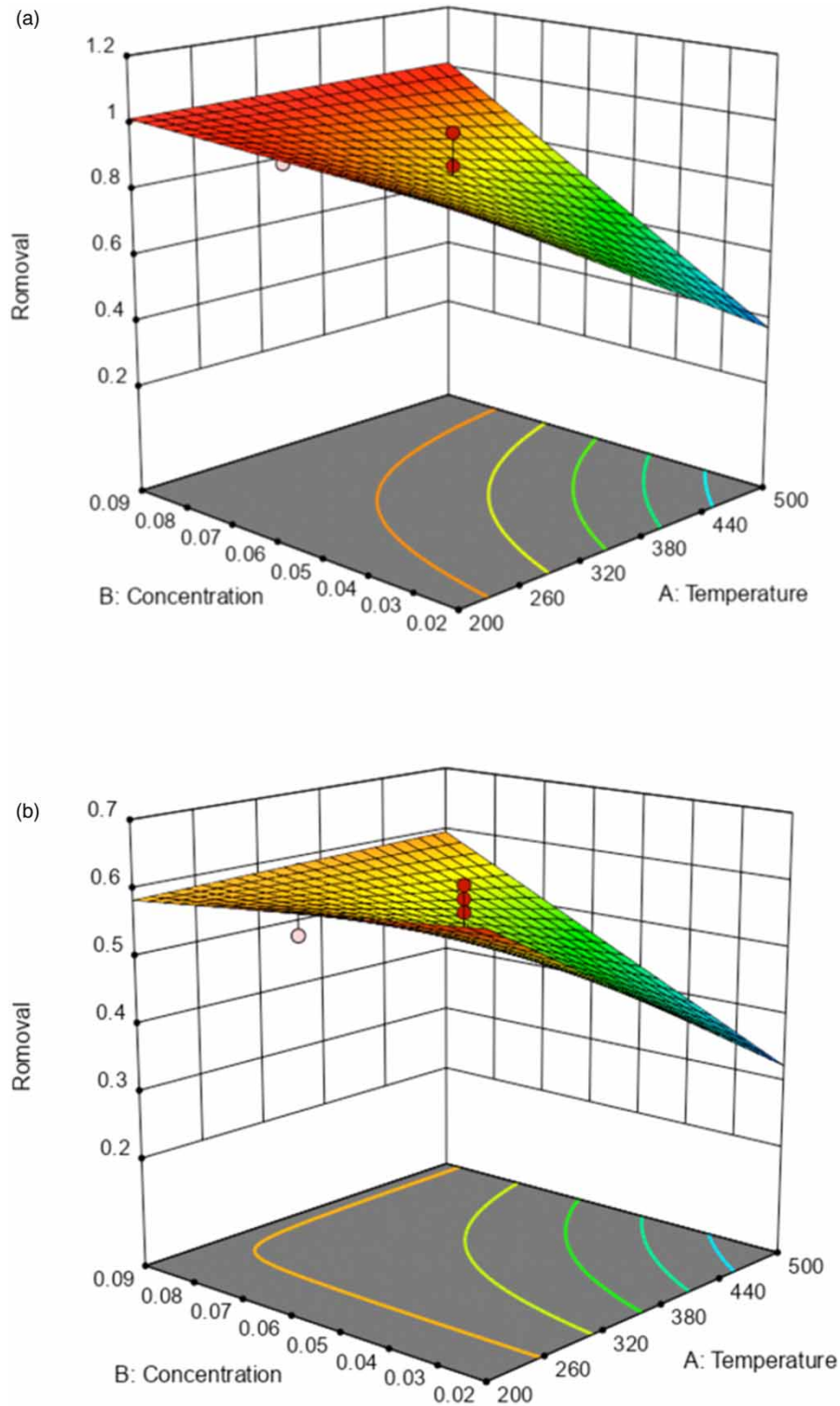


Figure 1 | Response surfaces plots showing the effect of process variables on MBTW production for (a) Cr(VI) removal and (b) total Cr removal at pyrolysis time 3 h.

The *P*-value for the Interaction Model shown in Table 2 was less than 0.0001, which indicated that this model adequately described the dependence of total Cr removal on the process variables. The most significant model terms were the same as the ones in Cr(VI) removal including the concentration of FeCl₃ solution, pyrolysis temperature and the interaction of the two factors. In addition, it was also found that the pyrolysis time did not have a significant effect on the total Cr removal. The effect of FeCl₃ concentration and pyrolysis temperature on the total

Cr removal was also investigated. As shown in Figure 1(b), it is interesting to see that the influence of the FeCl_3 concentration and pyrolysis temperature on the total Cr removal showed nearly the same trend as the ones on the Cr(VI) removal. For instance, when the FeCl_3 concentration 0.02 g/g was used, the total Cr removal decreased from around 60% to less than 35% with the increase of the temperature from 200 °C to 500 °C. Therefore, it is concluded that the high level of FeCl_3 concentration or the low pyrolysis temperature could result in the produced MBTW with a relatively higher removal percentage for both Cr(VI) and total Cr. As Cr(VI) is the most toxic compared to Cr with other valence states, based on the Cr(VI) removal percentage and also the energy consumption during the production process, the MBTW produced using pyrolysis temperature 200 °C, FeCl_3 concentration 0.055 g/g and pyrolysis time 3 h was selected for further characterisation and full adsorption studies.

3.2. The characterisation of MBTW

The FT-IR spectra of the MBTW before and after adsorption is illustrated in Figure 2. As shown in the figure, the bands at 1,020 and 1,084 cm^{-1} were due to the stretching of the C-O of the alcoholic groups (Saygılı *et al.* 2018). The peak at 1,150 cm^{-1} confirmed the presence of C-O of phenols. These groups can be involved in complexation reactions with the chromate ions. The band around 1,310 cm^{-1} could be assigned to C-O of aromatic ester, however, the band was absent in the MBTW after adsorption. The peak at 1,403 cm^{-1} represented the symmetric stretch of C – N. The bands observed at around 1,600 cm^{-1} were linked with the C-O stretching mode conjugate with the $-\text{NH}_2$ group (Oliveira *et al.* 2008; Wen *et al.* 2017; Saygılı *et al.* 2018). It is noticed that this band was shifted to a lower wavenumber in the MBTW after the adsorption process. Those carbonyl stretching peaks were found at 1,705 cm^{-1} (George *et al.* 2015). The bands observed at around 2,920–2,850 cm^{-1} were associated with stretching vibration of aliphatic C-H (Nebaghe *et al.* 2016; Wen *et al.* 2017; Chen *et al.* 2019). The peaks at 3,400 cm^{-1} were attributed to the bonded $-\text{OH}$ groups, but the bands became much weaker in the MBTW after the adsorption process. There reduction in these bands also indicate dominant complexation mechanism (Albadarin *et al.* 2013). The changes in the FTIR spectra of the adsorbent after interaction with the chromium ions suggests that removal of Cr(VI) from aqueous solution may be a chemisorption process involving interaction of chromate ions with the function groups on the adsorbent material. From the CHNS analysis, it is observed that the carbon, hydrogen and nitrogen content of the MBTW was 38.05%, 3.19% and 0.45%, respectively. The sulfur content was below 0.3%.

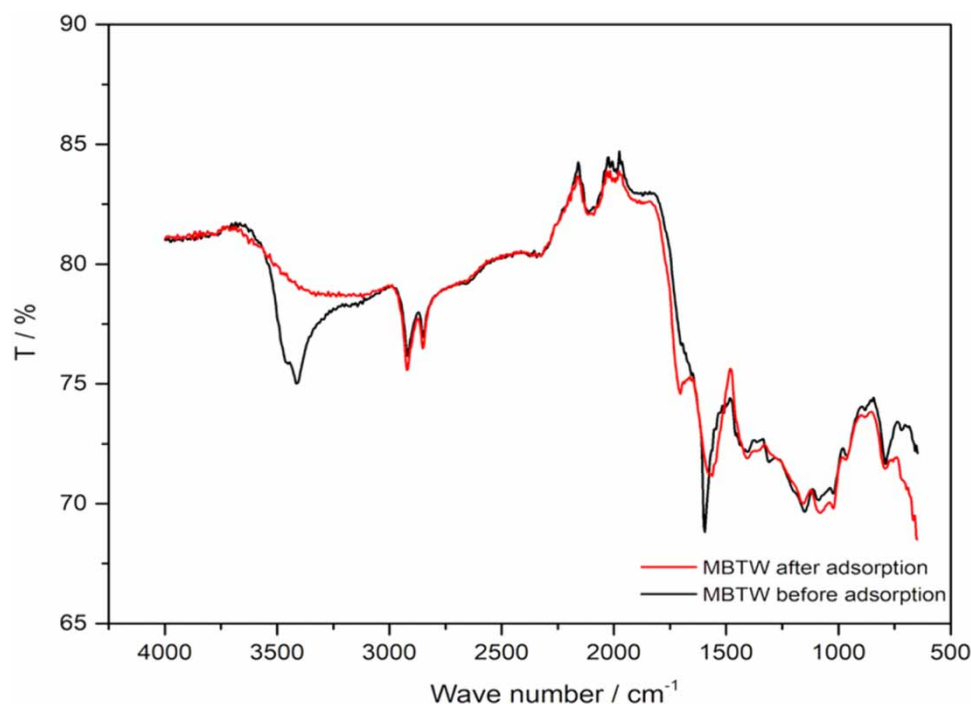


Figure 2 | The FT-IR spectra of the MBTW before and after adsorption experiment.

These textural properties of the MBTW adsorbent material are shown in Figure 3. It can be seen in Figure 3 that the surface morphology of the material is loose with curly structures and folds. These structures increased the surface area of the material and facilitate the biosorption of the adsorbate.

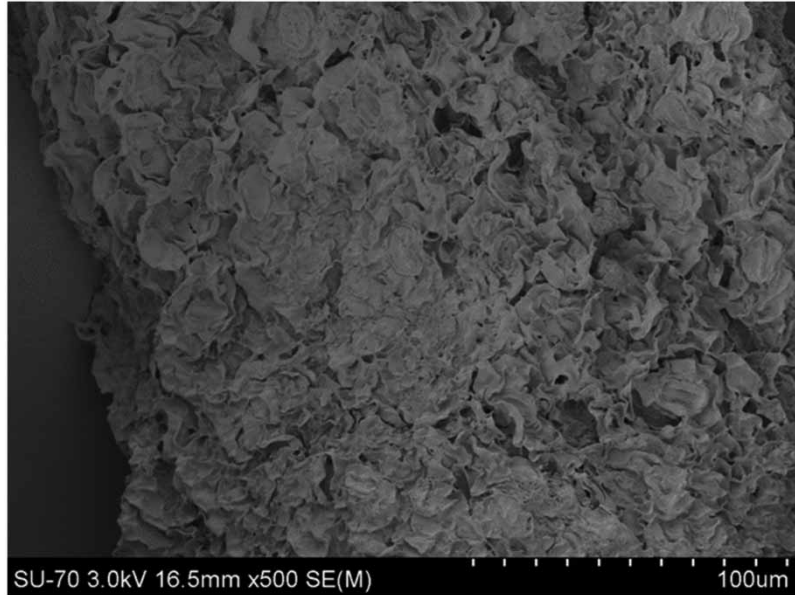


Figure 3 | SEM of MBTW used in the adsorption experiments. This was produced at a temperature of 200 °C and the duration of thermal treatment was 3 hr.

3.3. The effect of dosage

Different dosages 0.5 g/L, 2.5 g/L, 3.5 g/L, 5 g/L and 7.5 g/L of the MBTW were used in this study for Cr(VI) removal. After adsorption of 24 h, the results are illustrated in Figure 4. When the MBTW dosage applied increased from 0.5 g/L to 7.5 g/L, the Cr(VI) removal percentage increased from 26% to nearly 99%. A higher MBTW dosage means more surface area or exchangeable sites for adsorption, so the removal percentage of Cr(VI) would increase with the increasing adsorbent dosage. The observed increase in the removal efficiency as the dosage of the biochar used is in agreement with other reports from the literature (Chen *et al.* 2019; Mangwandi *et al.* 2020). The number of active sites responsible for reduction and adsorption of Cr(VI) is proportional to the amount of adsorbent used, hence increasing dosage improves the removal performance.

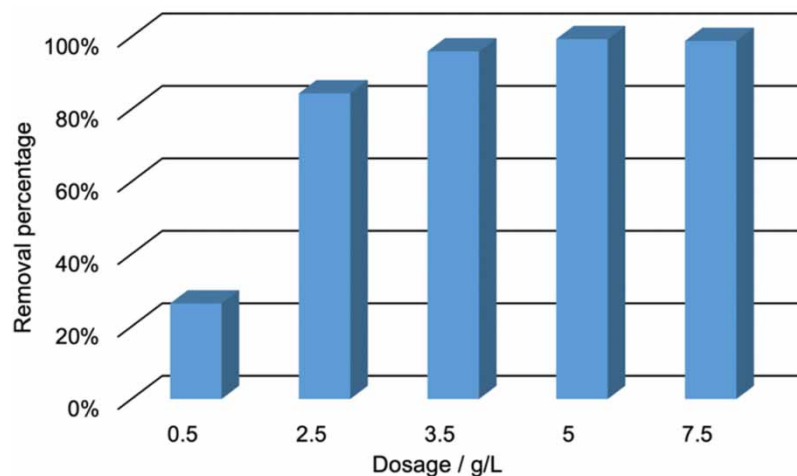


Figure 4 | The effect of MBTW dosage on the removal of Cr(VI).

3.4. The adsorption isotherms

Adsorption isotherm studies are important to describe the fraction of adsorbate molecules that are divided between solid and liquid phases at equilibrium. The Cr(VI) adsorption isotherms on the MBTW are illustrated in Figure 5. The Cr(VI) adsorption isotherms for the MBTW sample showed a large amount of uptake, removing nearly all the Cr(VI) at low concentration solutions. In the current study, the isotherm results were examined using the different isotherm models shown as below: Langmuir (5), Freundlich (6), Sips (7), Redlich-Peterson (8) and Temkin (9) (Nebaghe *et al.* 2016; Chen *et al.* 2019). Non-linear regression analysis was used to fit the adsorption isotherm models to experimental data.

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$q_e = \frac{q_{max}b_s C_e^m}{1 + b_s C_e^m} \quad (7)$$

$$q_e = \frac{q_{max}B_{pb} C_e}{1 + B_{pb} C_e^\beta} \quad (8)$$

$$q_e = B \ln(A \cdot C_e) \quad (9)$$

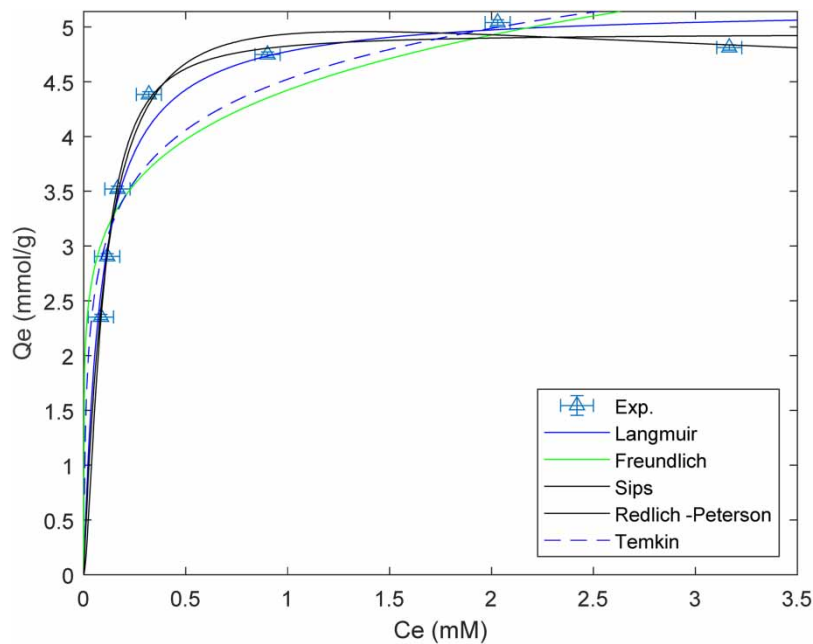


Figure 5 | The adsorption isotherms of Cr(VI) removed by the MBTW at 60 °C.

In Equations (5)–(9), where q_e is the removal capacity at equilibrium (mmol/g); q_{max} (mmol/g) is the maximum amount of Cr(VI) removed by the MBTW; K_L (L/mmol) and K_F ($[\text{mmol.g}^{-1}]/[\text{mmol.L}^{-1}]^{1/n}$) are the Langmuir constant related to the interaction bonding energies and the Freundlich affinity coefficient, respectively; C_e (mmol/L) is the equilibrium concentration of the Cr(VI) solution; b_s is the Sips isotherm affinity constant (L/mmol); B_{pb} is the Redlich-Peterson isotherm constant (L/mmol); β is an exponent that lies between 0 and 1; A is equilibrium binding constant (L/g); B is the constant related to the heat of the adsorption.

All the parameters obtained from adsorption isotherm models and regression coefficient R^2 are shown in Table 3. The Langmuir maximum removal capacities of the MBTW at 60 °C to Cr(VI) was above 5 mmol/g, which was about 1.6 times greater than that of the MBTW at room temperature (3.3 mmol/g).

Table 3 | Summary of the parameters of the isotherm models (60 °C)

Metal	Langmuir		Freundlich		the Sips		Redlich -Peterson		Temkin	
Cr(VI)	R ²	0.9614	R ²	0.7467	R ²	0.9912	R ²	0.9860	R ²	0.8091
	K _L	11.65	K _F	4.42	b _s	42.93	B _{pb}	8.04	A	853.93
	q _{max}	5.19	n	6.44	m	1.57	β	1.09	B	0.67
					q _{max}	4.94	q _m	5.55		

The maximum removal capacity of the MBTW was much higher than that of commonly used teawaste biosorbents reported by other researchers, which are shown in Table 4, indicating that the MBTW produced in this work could be used as an efficient and low-cost biosorbent for wastewater treatment of Cr(VI). Considering the R² value, the Sips model (R² = 0.9912) was found to fit the removal data better than the other models, which suggests that the removal of Cr(VI) on the MBTW might be controlled by multiple mechanisms. As for the total Cr, non-linear regression analysis was also used to fit different adsorption isotherm models shown above to the experimental data; however, all the regression coefficient R² results were lower than 0.7.

Table 4 | The Langmuir removal capacities of Cr(VI) by different biosorbents

Biosorbent	Pyrolysis T [°C]	Pyrolysis t [h]	Adsorption T [°C]	pH	q _m [mg g ⁻¹]	Reference
Teawaste (tea bag)	–	–	30	2	113.4	Albadarin <i>et al.</i> (2013)
Teawaste magnetic porous carbon	300	1	–	5	21.23	Wen <i>et al.</i> (2017)
Teawaste/Fe ₃ O ₄ composite	–	–	35	2	67.57	Fan <i>et al.</i> (2017)
Teawaste (local shop)	–	–	30	3.9	90.9	Mohit <i>et al.</i> (2019)
MBTW	200	3	RT	2	171.6	this work
MBTW	200	3	60	2	269.9	this work

RT, room temperature.

3.5. The thermodynamics

The thermodynamic parameters: standard Gibb’s free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for the removal of Cr(VI) by the MBTW were calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_c \tag{10}$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{11}$$

where R (8.314 J/mol K) is the universal gas constant; T (K) is absolute temperature; K_c (L/g) is the equilibrium constant at temperature T (q_e/C_e); C_e (mg/L) is the equilibrium concentration of the Cr(VI) solution; q_e (mg/g) is the amount of Cr(VI) removed by the MBTW at equilibrium.

All the thermodynamic parameters obtained are presented in Table 5. As shown in the table, both ΔH° and ΔS° were positive for the removal of Cr(VI) by the MBTW which implied the endothermic removal process and an increase in randomness at the solid/solution interface. Therefore, it is indicated that increasing the solution temperature would enhance the binding potential at equilibrium (Suksabye & Thiravetyan 2012). Similar results of

Table 5 | Thermodynamic parameters for adsorption of Cr(VI) by MBTW at different temperatures

ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)				
		RT	30 °C	40 °C	50 °C	60 °C
23.05	0.04	11.78	11.39	11.01	10.62	10.24

RT, room temperature.

Cr(VI) removal by the tea waste and date pits were reported by *Albadarin et al. (2013)*. For the removal of Cr(VI) by the MBTW produced, all ΔG° values were positive and the values decreased with the increase of the adsorption temperature, suggesting that this process was nonspontaneous and the process would become more spontaneous at higher temperatures.

3.6. The adsorption kinetics

As shown in *Figure 6*, initial rapid removal of Cr(VI) by the MBTW was observed during the first four hours, then followed by a slower process as the removal approached equilibrium. In beginning, the active sites on the surface of the MBTW were open and the Cr(VI) could easily contact the active sites, thus a quick removal rate could be seen. Pseudo-first-order (12), pseudo-second-order (13), Elovich (14) and modified Freundlich kinetic (15) kinetic models were used to determine the adsorption kinetic parameters as follows (*Fan et al. 2017*):

$$q_t = q_e(1 - e^{-k_1 t}) \quad (12)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (13)$$

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (14)$$

$$q_t = k_0 C_0 t^n \quad (15)$$

where q_t (mmol/g) and q_e (mmol/g) are the amounts of heavy metal adsorbed by the biochar at time t and at equilibrium; k_1 (1/min) and k_2 (g/mmol min) are the pseudo-first-order and pseudo-second-order apparent rate constant, respectively; α is the initial adsorption coefficient (mmol/g min) and β is the desorption coefficient (g/mmol). In Equation (15), C_0 is the initial concentration of adsorbate solution while n and k_0 are the model parameters.

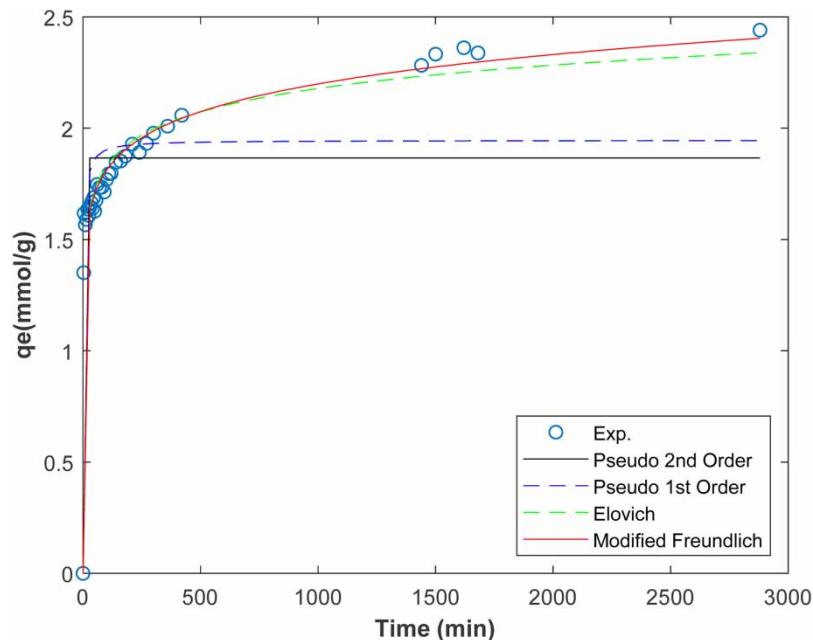


Figure 6 | Kinetics of Cr(VI) removal by the MBTW.

The non-linear kinetic fittings of Cr(VI) on the MBTW are shown in *Figure 6* and the fitting parameters of pseudo-first-order, the pseudo-second-order, Elovich and Modified Freundlich are shown in *Table 6*. Compared to the R^2 from the pseudo-first- and second-order kinetic models, the Elovich model had a better R^2 value 0.9693, indicating that the Elovich model could fit the Cr(VI) removal process well. It is noted that the Elovich model is

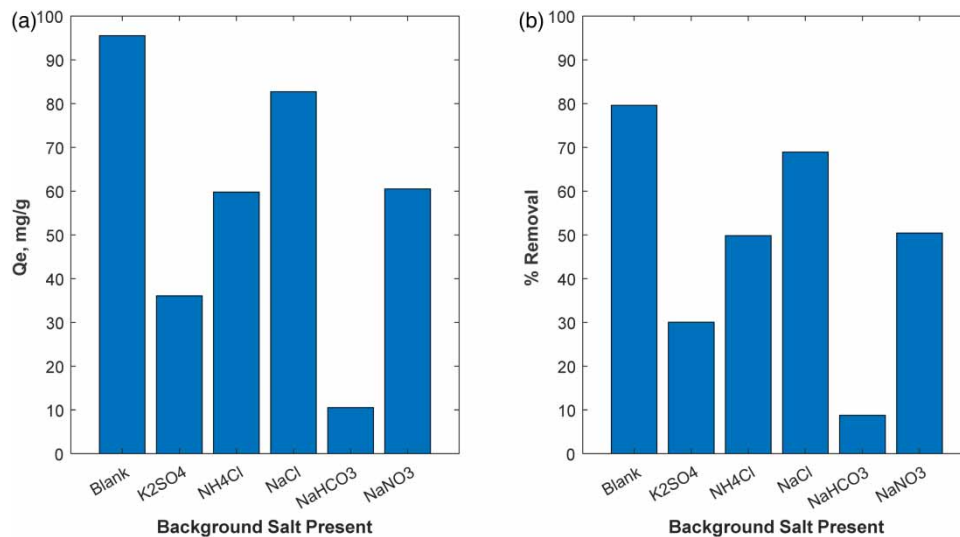
Table 6 | Kinetic model parameters of removal of Cr(VI)

Pseudo-first order			Pseudo-second order			Elovich			Modified Freundlich		
q_e	k_1	R^2	q_e	k_2	R^2	α	β	R^2	k	n	R^2
97.04	0.39	0.6566	101.15	0.004	0.7413	268.3	6.61	0.969	0.2161	0.0841	0.956

used to interpret the kinetics of chemisorption on highly heterogeneous adsorbents, suggesting chemisorption played an important role during the removal of Cr(VI) by the MBTW (Chien & Clayton 1980). The fact that Elovich model describes the kinetics data well further confirms the FTIR results presented earlier which show possible interaction of the chromate ions with functional groups on the adsorbent.

3.7. Effect of background salts on Cr(VI) removal

However, it must be noted that the removal of the metal Cr(VI) by the biosorbents can be influenced by the presence of other ion species as reported in the literature. For example, it was reported by Rathour *et al.* that the adsorption of Cr(VI) in binary and ternary association with Pb^{2+} , Cd^{2+} and Cl^- seemed unaffected (Rathour *et al.* 2020). The influences of various salts, such as NaCl, NH_4Cl , K_2SO_4 , $NaNO_3$, $NaHCO_3$, on the biosorption of Cr(VI) onto MBTW was investigated. It was found that the Cr(VI) removal onto date pits and olive stones decreased significantly in Figure 7 the presence of $NaHCO_3$ salt, which can be indicated that carbonate ions (CO_3^{2-}) as strongly compete with Cr(VI) for binding sites. Likewise, the Cr(VI) removal onto MBTW was significantly reduced by the presence of other salts, which can be due to the weak interaction between the negative and positive charge, leading to limitation of the approach between the biomass particles and Cr(VI) ions. The result was similar to the other works (Albadarin *et al.* 2013; Mangwandi *et al.* 2020). This information is vital when designing and sizing the separation units as it allows some adjustments to be made on the quantities of the adsorbent used to compensate for efficiency loss due to existence of other competing ions in solution.

**Figure 7** | Effect of background salts on Cr(VI) removal.

4. CONCLUSIONS

The MBTW materials were successfully produced for Cr(VI) removal. The results showed that both the concentration of $FeCl_3$ solution and pyrolysis temperature were significant factors in producing MBTW for Cr(VI) and total Cr removal. However, the pyrolysis time did not have a significant effect on both Cr(VI) and total Cr removal. A portion of Cr(VI) was found to be reduced to Cr(III) during the adsorption process, and the adsorption capacities of the MBTW could achieve 171.6 mg/g at room temperature. Further investigations on effect of

temperature on adsorption revealed that the Cr(VI) removal process was endothermic and chemisorption played an important role during the process. It can be concluded that the novel MBTW produced herein is an excellent biosorbent material for the efficient separation of toxic Cr(VI) from wastewater in environmental pollution areas even when at room temperature. The presence of other ions in solution was shown to negatively affect the removal of Cr(VI), carbonate ions were shown to have a huge effect. Therefore this must be taken into account when sizing the systems for removal of the Cr(VI) especially if carbonate ions are known to be in the aqueous solution to be treated.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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