Modelling and optimization of hexavalent chromium removal from aqueous solution by adsorption on low-cost agricultural waste biomass using response surface methodological approach

Boutheina Rzig, Fatma Guesmia, Mika Sillanpää, Béchir Hamrouni

Abstract

In this study, response surface methodology (RSM) approach using central composite design (CCD) was investigated to develop mathematical model and to optimize the effects of pH, adsorbent amount and temperature related to the hexavalent chromium removal by biosorption on peanut shells (PSh). The highest removal percentage of 30.28% was found by the predicted model under the optimum conditions (pH of 2.11, 0.73 g of PSh and 37.2 °C) for a 100 mg/L initial Cr (VI) concentration, which was very near to the experimental value (29.92%). The PSh was characterized by SEM, EDX, FTIR, BET, XRD analysis. Moreover, Langmuir isotherm fitted well ($R^2 = 0.992$) with the experimental data, and the maximum adsorption capacity was discovered to be 2.48 and 3.49 mg/g respectively at 25 and 45 °C. Kinetic data was well foreseen by pseudo second order. Thermodynamic study depicted that biosorption of Cr(VI) onto PSh was spontaneous and endothermic. Regeneration of the PSh using NaOH showed a loss <5% in the Cr (VI) removal efficiency till three recycle runs. In summary, the Cr (VI) removal onto economic, sensitive and selective biosorbent (PSh) optimized using CCD to study biosorption behaviors.

Key words: biosorption, hexavalent chromium, isotherm, kinetic, peanut shells, response surface methodology

Highlights

- Biosorption has been investigated as a solution for Cr (VI) removal from wastewater.
- Optimization of Cr (VI) removal on PSh through 3 factors central composite design.
- The highest removal yield was obtained for a pH of 2.11, adsorbent amount of 0.73 g and temperature of 37.2 °C.
- The maximum adsorption capacity was 3.5 mg/g. Cr (VI) adsorption followed Langmuir isotherm and pseudo-second-order kinetic models.
1. INTRODUCTION

Wastewater pollution by chromium is of major concern due to the excessive amount generated by various industries using processes that retain a chromium finish treatment, which is destructive to the environment and human health (Jobby et al. 2018). In fact, chromium is the 7th most abundant element on earth (Ponnusamy & Yashwanthraj 2017), which dispersed to the groundwater and surface water, due to its extensive use in various industrial sectors such as metallurgy, tanning industries, painting, ceramics and the production of steel and alloys owing to its various qualities such as hardness, solubility and corrosion resistance (Hamilton et al. 2018). Chromium has different oxidation states, the most stable of which are trivalent chromium Cr (III) and hexavalent chromium Cr (VI) (Mahmoud et al. 2020). Studies reveal that Cr (VI) is among the 14 most toxic chemicals posing threat to humans even at ppb concentrations (Pradhan et al. 2017). It can well penetrate into the body through skin, digestion, the respiratory tract and mucous membranes (Li et al. 2021). Moreover, the International Agency for Research on Cancer (IARC) classified Cr (VI) compounds as carcinogenic to humans (Moffat et al. 2018). The World Health Organization (WHO) recommended a maximum allowed concentration of Cr (VI) to 0.05 and 0.5 mg/L respectively in drinking water and industrial wastewater (Aigbe & Osibote 2020).

Several techniques were used for the uptake of this pollutant from aqueous systems including precipitation (Sun et al. 2007), electrocoagulation (Hamdan & El-Naas 2014), reverse osmosis (Mnif et al. 2017), ion exchange (Harbi et al. 2016) and adsorption (Jain et al. 2018), but these methods have several disadvantages such as high operational cost, high reagent and energy consumption, low selectivity, higher quantities of sludge generation, time consuming and labor-intensive (Iftekhar et al. 2017). Recently, the adsorption process, as an alternative treatments, has attracted the intensive attention to find low-cost adsorbents with high chromium removal capacities (Pakade et al. 2019). A large range of adsorbents have been studied, including carbon based materials, mineral, organic or biological origin, biosorbents, agricultural wastes. The low cost of agricultural wastes sorbents contrasted with conventional adsorbents inspired the researchers to exploit them as competent sorbents for

---

GRAPHICAL ABSTRACT

![Graphical Abstract](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.233/902360/wst2021233.pdf)
hexavalent chromium ions removal (Mondal et al. 2017). The agricultural products enclose some compounds, including lignin, pectin, cellulose, hemicellulose, which possess effective functional groups with great affinity to Cr (VI) ions (Ali et al. 2016). In addition, they have been used owing to their low cost, renewability, sustainability, rich surface with functional groups and biodegradability (Dai et al. 2018). Several studies were focused on the efficiency of various biosorbents for Cr(VI) removal such as potato peels (Mutongo et al. 2014), peapod (Sharma et al. 2016), rice straw (Gao et al. 2008), barks of acacia albida (Gebrehawaria et al. 2015), teff straw (Tadesse et al. 2014). Recently, agricultural wastes such as pineapple core (Rosales et al. 2019), tea (Çelebi 2020), sugarcane bagasse (Karri et al. 2020), mango kernel (Akram et al. 2017), phragmites australis and ziziphus spin-christi (Mahmoud et al. 2020), fruit peel (Ben Khalifa et al. 2019; Wang et al. 2020) showed good results in the adsorption of Cr (VI) ions. Nag et al. have studied the efficiencies of diverse natural biomaterials including mango, jackfruit, bamboo leaves, onion and garlic peel, coconut shell and acid-treated rubber leaf for Cr(VI) removal from aqueous solution. Their results showed maximum capacity of 35.7 mg/g for mango leaf and the sequence of adsorption capacity was found to be mango leaf > jackfruit leaf > acid-treated rubber leaf > onion peel > bamboo leaf > garlic peel > coconut shell, at a lower pH solution (Nag et al. 2020). Another study done by Rambabu et al. showed Cr (VI) removal efficiency of 58.02% using date palm empty fruit bunch wastes (Rambabu et al. 2020).

Peanut shells (PSh) are low-cost, abundant, inexpensive and available in huge quantities. According to the Food and Agriculture Organization of the United Nations, 46 million tons of peanut were produced worldwide in September 2019 (Sorita et al. 2020). Approximately, 1 kg of peanut generated about 250–300 g of shells and it has been predicted that 10.7–14.0 million tons of peanut shell waste were generated worldwide in the years 2017 and 2018 (Ge et al. 2020). In addition, the Tunisian Ministry of Agriculture announced that the production of peanuts increased from 5,060 to 6,495 tons from the year 2015 to 2019.

There are many ways and procedures to optimize the adsorption process. The traditional single-variation method is not a reliable method of finding optimal conditions. Currently, Response Surface Methodology with Central Composite Design (RSM-CCD) has been widely used in environmental study modeling and optimization processes (Badr et al. 2020). RSM-CCD is an empirical statistical technique that contributes to development, improvement and optimization processes and can simultaneously resolve the optimum of several variables with the least number of experiments providing an appropriate experimental design (Mondal et al. 2017). Numerous applications of RSM were successfully conducted to optimize the hexavalent chromium removal using biomaterials (Ben Khalifa et al. 2019; Afshin et al. 2021; Bian et al., 2021; Guo et al., 2021).

To the best of our knowledge, there are few studies relating to the biosorption of Cr (VI) onto PSh using RSM with Central Composite Design (CCD). The main novelty of the reported study is to evaluate the biosorption capacity of PSh biomass owing to the diverse functional groups present in it. Additionally, the work intends to expose the performance of CCD to model and optimize hexavalent chromium removal from aqueous solution by adsorption on PSh, which has not been established until now. Consequently, considered PSh as a low-cost, effectual and sustainable biosorbent for effective treatment of Cr(VI) ions polluted water.

The aims of this study were to recuperate the PSh wastes and reuse them for Cr (VI) removal from wastewater. The produced biosorption was characterized by (SEM), (EDX), (FTIR), (BET), (XRD) and also by using Boehm and pH zero charge methods. The significant variables (pH, adsorbent amount (g), and temperature (°C)) affecting Cr (VI) biosorption were studied and optimized using RSM with CCD according to the Desirability Function (DF). In addition, adsorption isotherms, kinetics and thermodynamic studies were processed in order to understand the adsorption mechanism. This work also reports recovery of Cr(VI) after adsorption process, which are necessary for sustainable application of peanut shells in wastewater treatment.

2. MATERIAL AND METHODS

2.1. Material

2.1.1. Reagents

A stock solution of hexavalent chromium (1,000 mg/L) was prepared by dissolving 2.828 g of potassium dichromate (K$_2$Cr$_2$O$_7$) of 99% purity obtained from Merck in 1 L distilled water. The complexing agent 1, 5-Diphenyldicarbazide (98%) was supplied by Sigma Aldrich. Hydrochloric acid (37%), sulphuric acid (95–98%) and ethanol (95%) were purchased from Acros. Sodium chloride and sodium hydroxide were obtained from Shamlab. All the solutions were prepared with distilled water.
2.1.2. Adsorbent preparation
The peanut shells (PSh) were collected from a local center of preparation of shell-removed peanut in Kelibia, Tunisia. The raw feed stocks were washed three times with tap water to remove all the adhering dirt. Then, they were washed three times with distilled water. The wet material was dried in the oven at 80 °C for 24 hours and was ground using a mortar. The resulting powdered PSh was sieved to obtain a particle size less than 250 μm. Table 1 shows some physical and chemical proprieties of peanut shells powder.

2.2. Methods
2.2.1. Characterization of the PSh
In this study, the morphology and structure of PSh were carefully investigated through various measurements. The surface functional groups of PSh were estimated by the Boehm method (Valentín-Reyes et al. 2019). This method is based on the neutralization of oxygenated functions by three bases having different strengths, sodium carbonate (Na₂CO₃), sodium bicarbonate (NaHCO₃) and sodium hydroxide (NaOH) in order to determine the nature and amounts of surface functionalities among carboxylic, phenolic and lactonic groups (Kim et al. 2012). 0.5 g of PSh was added to 50 mL of the three mentioned bases and HCl (0.1 mol/L). After 24 h, the basic functions were titrated with HCl (0.1 mol/L) and the acidic with NaOH (0.1 mol/L).

The pH of zero charge (pHpzc) was determined by mixing 0.15 g of PSh with a solution 0.01 mol/L NaCl. The pH of each sample was adjusted to different values from 2 to 12 (2 units increment) using HCl (1 and 0.1 mol/L) and NaOH (1 and 0.1 mol/L). After 24 h the final pH of solutions was measured and the point of intersection of pHfinal Versus pHinitial was noted as pHpzc of PSh. The pHpzc of a material refers to the pH value for which the net charge on the surface of the material is zero (Norouzi et al. 2018).

Fourier transform infrared spectroscopy (FTIR) of the PSh was conducted by Bruker Vertex 70 model, in a spectral range of 400–4,000 cm⁻¹. The PSh was also characterized by X-ray Diffraction (XRD Model: PANalytical X-ray diffractometer) to identify the surface groups and phase identification. Microstructure and morphology of the native PSh was carried out using Hitachi S-4800 scanning electron microscope (SEM) operating at 20 kV. The elemental composition of PSh was determined using Energy Dispersive X-ray Spectrometer (EDX). The surface area and pore size of the biosorbent was determined using nitrogen adsorption isotherms at 77 K recorded with a Micrometrics Surface Area Analyzer (ASAP 2020, Micrometrics Inc, USA) after degassing at 100 °C overnight.

2.2.2. Batch biosorption experiments
The adsorption experiments were performed to study the effect of various operating parameters on adsorption. Batch biosorption of Cr (VI) on PSh was carried out in erlenmeyer conical flask with constant time of 45 min and constant agitation speed of 125 rot/min. Adsorption tests were conducted to investigate the effects of solution pH (2.11–9.22), adsorbent amount (0.07–0.73 g) and temperature (12.70–37.20 °C) on the optimization of Cr (VI) adsorption on PSh. Solutions with different concentrations of hexavalent chromium in the range of 10–250 mg/L

Table 1 | Physical and chemical proprieties of peanut shells

| Parameters     | Wt % | Reference              |
|----------------|------|------------------------|
| Moisture       | 5.54 | This study             |
| Ash content    | 4.26 |                       |
| Total carbon   | 47.54|                       |
| Total hydrogen | 6.00 |                       |
| Total nitrogen | 3.24 |                       |
| Total sulfur   | 2.53 |                       |
| Total oxygen   | 41.77| Perea-Moreno et al. (2018) |
| Total chlorine | 0.07 | Sareena et al. (2014)  |
| Lignin         | 36.1 |                       |
| Hemicellulose  | 5.6  |                       |
| Cellulose      | 44.8 |                       |
| Volatile matter| 84.9 | Perea-Moreno et al. (2018) |
were prepared from the stock solution (1,000 mg/L). 50 mL of each solution was shaken at the same speed using a shaking water bath ‘OLS 200 Grant’. After filtration, the Cr(VI) concentration in the filtrate was determined by the 1, 5 diphenylcarbazide method using “VWR UV-1600PC” spectrophotometer at 540 nm. The percentage removal of Cr (VI) and the amount of adsorbed Cr (VI) \( q_e \) (mg/g) were respectively computed using the Equations (1) and (2):

\[
R\% \text{ Cr(VI)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}
\]

\[
q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{2}
\]

where \( q_e \) (mg/g) refers to the Cr(VI) adsorption capacity, \( C_0 \) and \( C_e \) (mg/L) are, the initial and equilibrium Cr(VI) concentrations respectively. Moreover, \( V \) (L) is the solution volume and \( m \) (g) is the adsorbent weight.

2.2.3. Statistical design of experiments

Experimental designs grant maximum efficiency using the smallest number of trials and, consequently the minimum cost. It is usually suitable for concurrent optimization of the effect of variables to improve the efficiency attributes and decrease errors with the least possible number of runs (Adio et al. 2017). Central Composite Design (CCD) as a broadly appropriate optimization method allows the approximation of coefficients in a mathematical form and predicts the reaction and the validation of method (de Carvalho et al. 2016). In this study, three factors \( pH \) \( (X_1) \), adsorbent amount \( (X_2) \) and temperature \( (X_3) \) were applied for hexavalent chromium removal percentage at five levels utilizing the STATISTICA 10.0 with 20 runs. Table 2 illustrates the experimental design points with the coded values of variables used in the matrix of experiments \((-1.68(\alpha), -1, 0, +1, +1.68(\alpha))\) having of 2 \( k \) axial points, \( 2^k \) factorial points and six central points. The central points were used to evaluate the data reproducibility and the experimental error. The second order polynomial model can be used to estimate the mathematical relation between the three independent variables by Equation (3) (Melliti et al. 2021):

\[
Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} b_{ij} X_i X_j + \varepsilon \tag{3}
\]

where \( Y \) refers to the predicted response (the percentage of Cr(VI) removal), while \( b_0 \) is the constant coefficient, \( b_i \) shows the linear coefficient, \( b_{ii} \) represents the quadratic, and \( b_{ij} \) shows the interactive coefficient. Moreover, \( X_i \) and \( X_j \) correspond to the independent variables; \( \varepsilon \) and \( k \) respectively represent the residual error and the number of the independent variables. The design was arbitrarily performed to reduce the effect of non-controlled variables. Furthermore, this design enables approximating quadratic effects and the main interaction. The Response Surface Methodology (RSM) was utilized to allow the considerable specification and assessment of the relative factors and resolve multivariate equation to acquire an optimum response. The modeling was conducted by adjusting the first or second order polynomial equations to the experimental reactions. Then, the variance analysis (ANOVA) was investigated to identify the essential effects of the variables and their interactions on the chromium removal process. Plotting tridimensional graph was performed to make the surface response used for predicting the optimum working conditions based on the \( p \)-value and \( F \)-value.

After the generation of polynomial model (Equation (3)), the desirability function (DF) was found to optimize the Cr (VI) adsorption process. The main advantages of DF are its ability to obtain qualitative and quantitative responses by simple and quick transformation of different responses for one measurement (Asfaram et al. 2015). The experimental response was converted to DF values, it is in the range of 0–1. The 1 indicates the maximum desirability and 0 the minimum desirability. Based on the study of S. Harbi et al., the DF equation can be expressed as follows (Harbi et al. 2016):

\[
DF_i = \left( \frac{U_i - \alpha}{\beta - \alpha} \right)^{w_i}, \quad \alpha \leq U \leq \beta
\]

\[
DF_i = 1, \quad U > \alpha
\]

\[
DF_i = 0, \quad U < \beta
\]

(4)
\( \alpha \) and \( \beta \) are the lowest and highest obtained values for the response \( U_i \) \((i = 1, 2, 3, \ldots, n)\) respectively, and \( w_i \) is the weight. The individual desirability scores for each predicted response are then combined on a single overall DF, which is calculated to find the optimum set of input variables as following:

\[
DF = \left[ df_1^{\alpha} \cdot df_2^{\alpha} \cdots df_n^{\alpha} \right]^{1/n}, \quad 0 \leq v_i \leq 1 \quad (i = 1, 2, 3, \ldots, n)
\]

\[
\sum_{i=1}^{n} v_i = 1
\]  

(5)

where \( df_i \) indicates the desirability of the response \( U_i \) and \( v_i \) represents the importance of responses.

2.2.4. Regeneration

Reusability of the biosorbent is very essential factor that influences the process economics of the biosorption system, precisely towards the operational costs of the process (Bharath et al. 2020). 0.73 g of PSb was treated with 100 mg/L of Cr (VI) solution for 45 min at the optimum conditions (pH (2.11) and temperature (37.2 °C)). Cr (VI) loaded adsorbent was filtered, dried overnight at 80 °C and transferred into a series of flasks containing 0.1 M of sodium hydroxide, 0.1 M of sodium chloride and distilled water. Saturated adsorbent was then agitated at 125 rot/min for 45 min with all desorption solutions. The temperature of 25 °C was chosen

| Code | Independent variables | Levels | \(-\alpha\) | \(-1\) | 0 | \(+1\) | \(+\alpha\) |
|------|-----------------------|--------|------------|--------|---|--------|--------|
| X_1  | pH                    | 2.11   | 3.63       | 5.75   | 7.88 | 9.22   |
| X_2  | Adsorbent amount (g)  | 0.07   | 0.20       | 0.40   | 0.60 | 0.73   |
| X_3  | Temperature (°C)      | 12.75  | 17.50      | 25.00  | 32.50| 37.25  |

Table 2 | Experimental setup for 5 levels, 3 factors surface response design, the experimental design matrix and responses (RSM) for Cr (VI) biosorption onto PSb

| Run order | X_1  | X_2  | X_3  | Experimental | Predicted |
|-----------|------|------|------|--------------|-----------|
| 1         | 5.75 | 0.40 | 25.00| 6.38         | 6.75      |
| 2         | 5.75 | 0.40 | 37.20| 10.05        | 10.27     |
| 3         | 7.88 | 0.20 | 32.50| 6.11         | 4.68      |
| 4         | 5.75 | 0.40 | 25.00| 7.15         | 6.75      |
| 5         | 5.75 | 0.07 | 25.00| 2.81         | 3.97      |
| 6         | 3.63 | 0.60 | 17.50| 13.01        | 14.63     |
| 7         | 5.75 | 0.40 | 25.00| 6.64         | 6.75      |
| 8         | 5.75 | 0.40 | 37.20| 7.40         | 6.75      |
| 9         | 7.88 | 0.60 | 17.50| 5.54         | 5.47      |
| 10        | 7.88 | 0.60 | 32.50| 8.22         | 8.14      |
| 11        | 5.75 | 0.40 | 25.00| 6.89         | 6.75      |
| 12        | 3.63 | 0.20 | 32.50| 15.83        | 16.09     |
| 13        | 3.63 | 0.60 | 32.50| 17.41        | 18.46     |
| 14        | 9.22 | 0.40 | 25.00| 4.85         | 6.48      |
| 15        | 3.63 | 0.20 | 17.50| 11.07        | 11.34     |
| 16        | 5.75 | 0.40 | 12.70| 4.70         | 4.21      |
| 17        | 7.88 | 0.20 | 17.50| 1.94         | 1.08      |
| 18        | 5.75 | 0.73 | 25.00| 10.98        | 9.54      |
| 19        | 5.75 | 0.40 | 25.00| 6.13         | 6.75      |
| 20        | 2.11 | 0.40 | 25.00| 26.29        | 24.56     |
for desorption experiments. The regenerated PSh was washed several times with distilled water, dried and applied for more Cr (VI) ions sequestration experiments.

3. RESULTS AND DISCUSSION

3.1. Adsorbent characterization

The intersection of the curve final pH = f (initial pH) with the bisector corresponds to the pH$_{pzc}$ of PSh as shown in Figure 1 was equal to 4.6. Therefore, when the pH of the solution is lower than 4.6, the adsorbent surface is charged positively. On the contrary, for pH values above 4.6, the surface is charged negatively (Raza et al. 2015).

The amounts of basic and acidic groups found in PSh are presented in Table 3. Obtained results proved that the adsorbent had more acidic functional groups at the surface. The distribution of the acidic functional groups differs: the carboxylic functions represent 31.03%, the phenolic functions 6.90% and the lactones 62.07%. These results are perfectly consistent with the pH of zero charge found previously (4.6). Omorogie et al. was found quit similar value for Nauclea Diderrichii seed biomass waste equal to 4.9 (Omorogie et al. 2016).

The FTIR spectrum of peanut shells is shown in Figure 2(a). The broad peak at 3,313 cm$^{-1}$ is an indicator of O-H group suggesting the presence of phenols and alcohols which proves the presence of cellulose and lignin in the PSh sample (Taşar et al. 2014). The peak observed at 2,922 cm$^{-1}$ is attributed to C-H stretching vibration of lignocellulosic components proving the presence of methyl and methylene groups (Ding et al. 2012). The peak situated at 1,724 cm$^{-1}$ was ascribable to carbonyl group C=O stretching vibrations of hemicelluloses. The absorbance peak at 1,627 cm$^{-1}$ is characteristics of aromatic C=O stretching vibrations in associated carbonyl of lignin. The peak around 1,509 cm$^{-1}$ may be attributed to C=C vibration of an aromatic cycles of lignin (Bayuo et al. 2019). The peak appearing in 1,030 cm$^{-1}$ indicates the presence of C=O bonds. The phenol (OH), Carbonyl (C=O) and carboxylic (COOH) groups are essential sorption sites (Lugo-Lugo et al. 2012). The existence of –OH group coupled to carbonyl group, confirms the presence of carboxylic acid groups in the biomass (Chigondo et al. 2013). The slight shifting of bands after adsorption of Cr (VI) ions is due to the chemical interaction confirming the sorption of PSh to chromium ions from wastewater (Banerjee et al. 2019). Zhao et al. (2020) reported a FTIR spectrum of peanut shells presenting similar bands.

XRD patterns of the material was determined by X-ray diffraction using a PANalytical X-ray diffractometer applying CoKα irradiation (λ = 1.79 Å) operated at 40 kV and 30 mA. The scanning scope and scanning speed were 10°-120°. The XRD pattern (Figure 2(b)) of peanut shells showed typical spectrum of cellulosic material having main and secondary peaks at 2θ of 24° and 16°, respectively. The major peak is an indicator of the presence of highly organized crystalline cellulose, while the minor rather weak peak is an indicator of a less organized polysaccharide structure (Zhu et al. 2009). The intensity of these peaks depends on the amount of cellulose present in the biomaterials (Prithivirajan et al. 2016). The conclusion is accordant with that of the FT-IR analysis.

Figure 1 | pH of zero charge of the PSh.

Table 3 | Acidic and basic surface groups for PSh

| Groups | Carboxylic groups | Lactonic groups | Phénolic groups | Total Acidic | Total Basic |
|--------|------------------|----------------|----------------|--------------|------------|
| Amount (mmol/g) | 0.9 | 0.2 | 1.8 | 2.9 | 1.6 |
The SEM micrographs of peanut shells at different magnifications were shown in Figure 3. As presented in Figure 3(a), the surface of PSh is porous, irregular and has different shapes. Inside the peanut shells matrix, a great numbers of pores were observed at higher magnification (Figure 3(c)). A variety of shapes were also observed, for example spiral tubes shapes (Figure 3(b-1)) and cavities (Figure 3(b-2)). These biomasses formed a unique and natural porous arrangement during plant growth. The surface of the PSh after the adsorption of Cr (VI) (Figure 3(d)) turned to be less porous on the PSh surface, indicating successful loading of Cr (VI) molecules on the PSh surface (Jawad et al. 2020a).

The EDX spectra results and the weight percentages (wt. %) of PSh are given in Figure 2(c). The amounts of C and O loaded on the surface with weight percentages of 68.68% and 30.01% respectively are rather high compared to Na, Mg, Cl and Ca loading. The Nitrogen adsorption-desorption isotherms of PSh was also obtained and shown in Figure 2(d), The isotherm is type-IV with broad H3 hysteresis loop as defined by the International Union of Pure and Applied Chemistry (IUPAC) classification (Thommes et al. 2015), which is characteristic of mesoporous materials. The specific surface areas pore volume and pore size of PSh was calculated to be 0.8126 m²/g, 0.0020 cm³/g and 8.9339 nm, respectively. Taşar et al. was studied the removal of lead (II) on peanut shells and was found similar surface area of 0.8444 m²/g, and average pore diameter of 20.72 Å using a Micromeritics ASAP 2020 apparatus. The pore volume was calculated as 0.000471 cm³/g (Taşar et al. 2014).

3.2. Preliminary adsorption experiments

3.2.1. Effect of contact time

Contact time was evaluated as one of the most essential factors affecting the biosorption efficiency. The Figure 4(a) showed that the Cr (VI) adsorption increased over time until reaching equilibrium after 45 minutes. The fast adsorption in the beginning is due to the availability of a high number of empty sites, and then the saturation is due to the saturation of adsorbent sites. Therefore, the optimum contact time was chosen as 45 min for
further experiments. Taşar et al. was evaluated the removal of Pb (II) on peanut shells and was found same optimum contact time (Taşar et al. 2014).

3.2.2. Effect of adsorbent amount

The effect of adsorbent amount was studied to get an idea about the range which is used for the experimental design. It can be seen in Figure 4(b) that the % Cr (VI) removal increased gradually from 4.05 to 22.33% with the increase in the mass of the adsorbent from 0.05 to 0.7 g and remained practically constant at adsorbent quantities higher than 0.7 g. This is due to the increase in the contact area and the number of adsorption sites and thus making easier penetration of Cr (VI) to the adsorption sites. Since the quantity of hexavalent chromium ion is stable, a raise in the amount of adsorbent over a quantity that can completely adsorb the available Cr (VI) had no clear effect on further enhance of percent adsorption.

Figure 3 | SEM images of PSh (a–c) before (d) after adsorption of Cr (VI).
3.3. The statistical experimental design

3.3.1. Statistical analysis and fitting of the model

Response surface methodology was developed by taking into consideration all the significant interactions in the CCD to optimize the critical variables and clarify the response surface nature in the experiment. The results of analysis of variance (ANOVA) and regression coefficients suggest the significant nature of contribution of the quadratic model with p less than 0.05.

In addition, the Lack of Fit (LOF) is the difference of the values around the model fitted to experimental values. LOF is an exacting experiment for adequacy of model fit with no influences of extra higher-order terms. The inefficiency of this model for fitting the data results in significant value. The \( P \)-value of LOF is \( 4.2 \times 10^{-5} \) (Table 4), verifying the fitting applicability of this method for well-fitting of the response. The validity of the polynomial model was checked by completing the coefficient of determination (\( R^2 \)). The large values of \( R^2 = 0.972 \) and adjusted \( R^2 = 0.947 \) indicate that the data predicted by the model correlated well with what is found experimentally. The Equation (4) was used to estimate the influence of the factors studied on the removal of chromium by adsorption on PSh:

\[
\begin{align*}
\text{R}\% \text{ Cr(VI)} &= 6,736 - 5, 143 X_1 + 1, 689 X_2 + 1, 856 X_3 + 3, 059 X_1^2 + 0, 003 X_2^2 \\
&+ 0, 188 X_3^2 + 0, 273 X_1 X_2 - 0, 288 X_1 X_3 - 0, 231 X_2 X_3
\end{align*}
\]

(6)

### Table 4 | Analysis of variance (ANOVA) and multiple regression results of the response surface quadratic model for the prediction of Cr (VI) removal onto PSh

| Source       | Sum of Squares | Degrees of freedom | Mean Square | F-Value | P-value | Prob > F |
|--------------|----------------|--------------------|-------------|---------|---------|----------|
| Model        | 464.3          | 3                  | 154.8       | 16.16   | <0.0001 |          |
| \( X_1 \)    | 359.0          | 1                  | 359.0       | 209.2   | <0.0001 |          |
| \( X_2 \)    | 38.4           | 1                  | 38.4        | 22.4    | 0.0008  |          |
| \( X_3 \)    | 46.0           | 1                  | 46.0        | 26.8    | 0.0004  |          |
| \( X_1 X_2 \)| 0.6            | 1                  | 0.6         | 0.3     | 0.5694  |          |
| \( X_1 X_3 \)| 0.7            | 1                  | 0.7         | 0.4     | 0.5475  |          |
| \( X_2 X_3 \)| 0.4            | 1                  | 0.4         | 0.2     | 0.6284  |          |
| \( X_12 \)   | 133.4          | 1                  | 133.4       | 77.7    | <0.0001 |          |
| \( X_{22} \) | 0.0            | 1                  | 0.0         | 0.0     | 0.9994  |          |
| \( X_{32} \) | 0.5            | 1                  | 0.5         | 0.3     | 0.6143  |          |
| Residual     | 153.3          | 16                 | 9.6         | –       | –       | –        |
| Lack of Fit  | 16.0           | 5                  | 3.2         | 14      | 0.0057  |          |
| Pure Error   | 1.1            | 5                  | 0.2         | –       | –       | –        |
| Cor Total    | 617.6          | 19                 | –           | –       | –       | –        |
where $X_1$, $X_2$ and $X_3$ respectively refer to the real values of the independent variables related to pH, adsorbent amount and temperature.

A Pareto chart was used mainly to recognize the factors that have the most cumulative effect on the system and thus abandon the less significant factors (Figure 5(a)). The frequency or impact of parameter is indicated by the length of each bar in the diagram. The positive coefficients indicate a desirable effect on the efficiency of Cr (VI) removal while the negative coefficients for the model indicate an undesirable effect. It can be seen from Figure 5(a) that the pH was the most influencing factor on the removal of chromium followed by the temperature and the adsorbent amount (Mahmoud et al. 2016). The signs of coefficients showed that the adsorbent amount and the temperature had positive effects, while the pH had a negative effect on the chromium removal.

The adequacy graph of the model (Figure 5(b)) prove that the experimental results (R %) are very close to the values calculated by the model, insuring an accuracy of the model for favorable and real prediction of the results. It is clear that there is no obvious pattern followed in the observed values versus the residuals (Figure 5(c)). Figure 5(d) presents the histogram of raw residual, in which the arbitrary template of the residuals as well, announces the adequacy of the model.

3.3.2. The effects of variables on Cr(VI) adsorption efficiency

To make easy the determination of the interactions between the factors and the identification of the main factors influencing the response, we resorted to the use of 3D surface plots (Fakhri 2014). The factors were taken in our case two by two in each figure while the third variable is maintained at level zero (in coded term). These plots are presented in Figure 6. From these interaction plots, it is noticed that there are very slight curvatures between the factors studied (pH, adsorbent amount and temperature) which affirm that there are very slight interactions between these factors, as it had already been shown by the statistical analysis of Pareto. Figure 6(a) shows the interaction connecting pH and adsorbent amount in the adsorption process of chromium on PSh. As shown,
the removal percentage of Cr (VI) sharply increases by decreasing pH (from 10.0 to 2.0). For pH less than 2.5 (Figure 6(a)), the adsorption efficiency was maximum. This can be explained by chromium species distribution and the pH of zero charge (pHPZC) of the biomass. At lower pH (pH < pHPZC), the HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ ions are the predominant chromium species and the surface of biosorbent gets positively charged (Haroon et al. 2016). Therefore, the improvement of the Cr (VI) uptake at lower pH could be due to the electrostatic attraction between the biosorbent surface and the chromium species in solution. In contrary at higher pH (pH > pHPZC), there is an electrostatic repulsion between the CrO$_4^{2-}$ ions present mainly in the solution and the surface of the adsorbent charged negatively.

Similarly, Figure 6(c) presents the effect of adsorbent amount and temperature on Cr (VI) removal while pH is constant. A grow in both adsorbent mass and temperature increased the percentage of Cr (VI) removal awaiting the optimum conditions were reached. Indeed, the number of abundant bonding sites on the PSh surface increased when adsorbent was added which caused the improvement of the chromium adsorption efficiency. The removal yield was better for the higher temperatures (Figure 6(b) and 6(c)). This result indicates that the Cr (VI) uptake on PSh is an endothermic in nature. The increasing in removal yield of Cr (VI) at high temperature can be attributed to the effect of temperature on the internal structure of the PSh, thus facilitation the diffusion of Cr (VI) ions in the PSh interspaces structure (Jawad et al. 2020a). Ben Ali et al. (2017) outlined that the biosorption on pomegranate peels was endothermic. The increase of adsorption efficiency with temperature suggests that active sites at the surface of the adsorbent available for adsorption increased with temperature. It may possibly also lead to some changes of the pore size which becomes larger and to a relative increase in the diffusion of the chromium ions due to the solution viscosity decreasing.
3.3.3. Optimum conditions
Maximum adsorption efficiency for Cr (VI) by PSh and the corresponding optimal experimental conditions were determined by the desirability function (Asfaram et al. 2017) (Figure 7). The profile for predicted values and DF developed by STATISTICA 10.0 software. The measure in the range of 0.0 (unpleasant) to 1.0 (very pleasant) was employed to obtain a global function (D) which must be maximized based on the efficient optimization and selection of the considered variables. As claimed by the results of the CCD design matrix in Table 2, the minimum and maximum Cr (VI) removal are respectively are equal to 1.94% and 26.29%. In conformity with these values, desirability function (DF) settings for each removal percentage as dependent factor are shown on the right side of Figure 7. The optimal conditions for chromium removal are a pH equal to 2.11, an adsorbent mass of 0.73 g and temperature of 37.2 °C. The maximum chromium removal percentage obtained from DF is 30.28%.

To verify the results given by the model, the experiment was repeated three times using the optimal conditions given by the software. The results showed an average Cr(VI) adsorption efficiency of 29.49 ± 0.8% which is near to the predicted value as revealed in Figure 7.

3.4. Mechanism of the biosorption of Cr (VI) on PSh
The biosorption mechanism of Cr (VI) ions on PSh surface associated perplexing adsorption chemistry with coexistence of several interactions. Generally, four main steps explain the mechanism of the biosorption of Cr (VI) ions at the surface of biosorbents rich in lignocellulose and hemicellulose. These steps are: (1) adsorption coupled reduction, (2) an anionic adsorption, (3) reduction and cationic adsorption and (4) cationic and anionic adsorption (Fan et al. 2017). Based on the PSh characterizations and the biosorption experiments obtained, a possible biosorption mechanism for the Cr (VI) ions removal by PSh could be planned through the adsorption-coupled reduction pathway.

Figure 8 describes the hexavalent chromium biosorption mechanism on PSh surface. The different surface functionality of PSh which contained various functional groups such as –OH, –NH₂, –COO, –COC, C=C (as showed through FTIR analysis) played a main role in the adsorption-coupled reduction mechanism. The mechanism suggested three main steps for the capture of Cr (VI) ions from the bulk phase to the solid phase. Thus, the
first step implicated the rapid adsorption of the Cr (VI) ions on these functional sites on the PSh surface by electrostatic attraction, following a surface protonation of PSh sites (Islam et al. 2019). Moreover, surface complexation facilitated the Cr (VI) ions uptake by the PSh sorbent owing to the presence of carboxyl groups. Besides, the adsorbed Cr (VI) ions on the PSh sustained a heterogeneous redox reaction to form Cr (III) ions, as represented by the Equation (7) (Fan et al. 2017):

$$\text{HCrO}_4^- + 7 H^+ + 3e^- \rightarrow \text{Cr}^{3+} + 4 \text{H}_2\text{O} \quad (7)$$

The strongly acidic medium provided an excess of $H^+$ ions for the reduction of chromium from its Cr (VI) nature to the Cr (III) state. Lastly, the reduced Cr (III) was more efficiently attracted to functional sites by electrostatic attractions and surface complexation. The greater affinity of Cr (III) ions for active anionic sites on the surface of the PSh improved the anchoring of chromium ions on the PSh biosorbent (Islam et al. 2019).

### 3.5. Adsorption equilibrium modeling

Adsorption isotherms were employed using four different models in order to elucidate the biosorption performance. Generally, adsorption isotherms including Langmuir, Freundlich, Dubinin–Radushkevich and Temkin present precious information about adsorption process, surface properties and adsorbent tendency. The adsorption experiments were conducted at four temperatures 283, 298, 308 and 318 K and for chromium concentration in the range of 10–250 mg/L. The Cr (VI) adsorption isotherms on peanut shells provided by the origin Pro version 8 software are represented in Figure 9. The non-linearized equations with the corresponding constants presented in the literature (Surip et al. 2020) are summarized in Table 5.

The chi-square test $\chi^2$ is a statistical tool used to recognize well between the adopted models because of the small difference between their regression coefficients was calculated according to the Equation (8) (Appa et al. 2019):

$$\chi^2 = \sum \frac{(q_{e,\text{exp}} - q_{e,\text{cal}})^2}{q_{e,\text{cal}}} \quad (8)$$

According to the values of $R^2$ and $\chi^2$ in Table 5, Langmuir model was the model which had the highest values of correlation coefficients $R^2$ which represents an excellent regression; in addition it had the lowest values of the chi-square $\chi^2$ at different temperatures. Therefore, Langmuir model was the most suitable model to describe the biosorption phenomenon of hexavalent chromium on PSh. This proved that the biosorption of Cr (VI) on PSh involved monolayer adsorption on the active sites of the material (Khammour et al. 2021).
In order to predict whether the adsorption process is favorable or unfavorable, the separation factor $R_L$ was calculated by Equation (9) (Rangabhashiyam et al. 2019):

$$R_L = \frac{1}{1 + C_0 K_L}$$  

were $C_0$ (mg/L) refers to the initial concentration of chromium and $K_L$ (L/mg) represent the Langmuir constant.

The $R_L$ values allowed a prediction of the shape of the isotherm and the nature of the adsorption process. For a favorable adsorption (Mahmoud 2020), $0 < RL < 1$, while $RL > 1$, $RL = 1$ and $RL = 0$ represent unfavorable monolayer adsorption process, linear [51], and irreversible adsorption process, respectively (Ali et al. 2019).

According to the calculated results of separation factor in Table 6, it can be seen that the values of $R_L$ are between 0 and 1, which proved that the adsorption of chromium on the peanut shells was favorable. Besides, the $R_L$ values decreased with the increase of the initial concentration, which showed that the adsorption was favorable for high initial concentrations.

The values of the Freundlich constant $n_F$ shown in Table 6 decreased with the increase of temperature, which implied a decrease in adsorption intensity. Moreover, the values of $1/n_F$ were less than unity, indicating favorable adsorption of chromium under the conditions studied. The value of the adsorption energy $E$ (kJ/mol) determined by the model D-A can be used to expect the adsorption process nature; it is given as follows by Equation (10):

$$E = \frac{1}{\sqrt{2}} K_{DA}$$  

Figure 9 | Plot of Langmuir, Freundlich, Dubinin-Astakhov and Temkin at 283 K (a), 298 K (b), 308 K (c) and 318 K (d) for chromium adsorption onto PSh ($\text{Cr (VI)} = 10$–$250$ mg/L, adsorbent amount = 0.73 g, V = 50 mL, pH = 2.11 and contact time = 45 min).
Physisorption occurs in the range of 1–8 kJ/mol, while for values more than 8 kJ/mol, chemisorption is ruling (Touihri et al. 2021). The values of E in Table 5 indicated the physical adsorption of Cr (VI) on PSh. In addition, the values of the heterogeneity factors nD were higher than 3 proved the homogenization of the adsorbent sites. On the other hand, as seen from Table 5, the adsorption heat bT of the Temkin model increased with the increase of temperature from 283 to 318 K proving that Cr (VI) adsorption on PSh was endothermic.

The performance of different adsorbents and their maximum Cr (VI) adsorption capacity is presented in Table 6. The Tunisian peanut shells have a relatively high adsorption capacity (3.489 mg/g) compared to other biomasses, confirming the suitability of the suggested use of PSh for the removal of Cr(VI). PSh proved a good adsorption capacity compared to some activated biomasses such as banana peel (Ali & Saeed 2015), barks of Acacia albida (Gebrehawaria et al. 2015) and leaves of Eucleas Chimperi (Gebrehawaria et al. 2015). The present biosorbent was able to remove 30.28 mg/L of Cr (VI) from wastewater which is a high concentration removal compared to other biomasses.

Many connections for binding Cr (VI) to the surface of PSh might be explained by one or more of these bonds as follows: (I) Electrostatic interaction of the chromium metal with charged surfaces on the PSh, (II) Surface area, total pore volume and pore size obtained by such kind of biomass, and active sites including and -OH and -COOH groups in PSh play an important role in chromium removal process.

### Table 5

| Isotherm model | Equation | Parameters | Value | Value | Value | Value |
|---------------|----------|------------|-------|-------|-------|-------|
| Langmuir      | \( q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \) | \( K_L \), \( 10^{-2} \) (L/mg) | 3.119 | 2.578 | 2.548 | 2.486 |
|               | \( q_m \) (mg/g) | 1.383 | 2.478 | 3.015 | 3.489 |
|               | \( R^2 \) | 0.990 | 0.992 | 0.991 | 0.992 |
|               | \( n_r \) | 0.002 | 0.004 | 0.007 | 0.009 |
| Freundlich    | \( q_e = K_F C_e^{\frac{1}{n_F}} \) | \( K_F \) (L/mg) | 0.197 | 0.277 | 0.333 | 0.368 |
|               | \( n_F \) | 2.899 | 2.583 | 2.563 | 2.507 |
|               | \( R^2 \) | 0.895 | 0.928 | 0.965 | 0.970 |
|               | \( n_D \) | 0.017 | 0.040 | 0.027 | 0.032 |
| Dubinin- Astakhov | \( q_e = q_{DA} \exp\left[-\left(\frac{E}{2RT}\right)^{n_D}\right] \) | \( q_{DA} \) (mg/g) | 1.264 | 2.211 | 2.659 | 3.083 |
|               | \( n_D \) | 4.444 | 4.445 | 4.577 | 4.502 |
|               | \( E \) (kJ/mol) | 2.130 | 2.093 | 2.049 | 2.083 |
|               | \( R^2 \) | 0.985 | 0.970 | 0.934 | 0.941 |
|               | \( n_D \) | 0.003 | 0.021 | 0.065 | 0.079 |
| Temkin        | \( q_e = \frac{RT}{b_T} \ln(K_T C_e) \) | \( b_T \) (J/mol) | 0.323 | 0.352 | 0.379 | 0.396 |
|               | \( K_T \) (L/mg) | 8,063.646 | 4,815.498 | 4,441.820 | 4,048.680 |
|               | \( R^2 \) | 0.973 | 0.983 | 0.980 | 0.974 |
|               | \( n_D \) | 0.004 | 0.009 | 0.016 | 0.027 |
|               | \( q_{ce,exp} \) (mg/g) | 1.024 | 1.811 | 2.015 | 2.237 |

### Table 6

| Chromium concentration (mg/L) | RL | Value | Value | Value | Value |
|-------------------------------|----|-------|-------|-------|-------|
|                               | 283 K | 298 K | 308 K | 318 K |
| 10                            | 0.762 | 0.795 | 0.797 | 0.801 |
| 25                            | 0.562 | 0.608 | 0.611 | 0.617 |
| 50                            | 0.391 | 0.437 | 0.440 | 0.446 |
| 80                            | 0.286 | 0.326 | 0.329 | 0.335 |
| 100                           | 0.243 | 0.279 | 0.282 | 0.287 |
| 200                           | 0.138 | 0.162 | 0.164 | 0.167 |
| 250                           | 0.114 | 0.134 | 0.136 | 0.139 |
3.6. Adsorption kinetics modeling

The kinetic experiments of Cr (VI) removal were analyzed using the non-linear form of the pseudo-first-order, pseudo-second-order and Elovich models (Huynh et al. 2020; Mohammed et al. 2020). The kinetics of PSh data obtained from the experiments of concentration of 100 mg/L at various contact times, and optimum conditions obtained previously along with the equations and constants are shown in Table 8. In addition the non-linear plots of the three models are illustrated in Figure 10.

As shown in Table 8, the pseudo second order kinetic model has the lowest chi-square value $\chi^2$ and the highest correlation coefficient $R^2$ comparing with the other models (first order and Elovich). So the pseudo second order model indicated excellent applicability for describing the chromium (VI) adsorption process on peanut shells. In addition, the values of the calculated $q_e$ from the pseudo second order model was close to the values of the experimental $q_{e,\text{exp}}$ suggesting that the Cr (VI) adsorption may be due to electrostatic attraction between the positively

### Table 7 | Comparison of maximum adsorption capacity of various adsorbents for Cr (VI) adsorption

| Biosorbent                   | Time (min) | pH  | Dosage (g/L, ga) | T (°C) | [Cr (VI)] mg/L | q_{max} (mg/g) | Removal efficiency (%) | References                  |
|------------------------------|------------|-----|------------------|--------|----------------|----------------|------------------------|-----------------------------|
| Teff straw                   | 60         | 2   | 0.6 (a)          | 25     | 5              | 3.51           | 79.9                   | Tadesse et al. (2014)       |
| Erythrina variegata orientalis leaf | 180       | 2.85| 50               | 30     | 90             | 1.92           | 99.1                   | Aditiya et al. (2012)       |
| Potatoes peel                | 48         | 2.5 | 4                | 25     | 40             | 3.28           | 95.31                  | Mutong et al. (2014)        |
| Modified Banana peel         | 60         | 6   | 4                | 25     | 400            | 3.35           | 96                     | Ali & Saeed (2015)          |
| Pea pod                      | 60         | 2   | 10               | 28     | 30             | 4.33           | 90                     | Sharma et al. (2016)        |
| Orange peel                  | 300        | 2   | 22.4             | 34.17  | 10             | 7.14           | 97                     | Ben Khalifa et al. (2019)   |
| Modified Barks of Acacia albida | 60        | 2   | 20               | 25     | 10             | 2.98           | 95.36                  | Gebrehawaria et al. (2015)  |
| Modified Leaves of Euclea-schimperi | 60        | 2   | 20               | 25     | 10             | 3.95           | 95.92                  | Gebrehawaria et al. (2015)  |
| Pineapple core               | 1,440      | 2   | 30               | 30     | 50             | 8.8            | 92.39                  | Rosales et al. (2019)       |
| Rice straw                   | 2,880      | 2   | 10               | 45     | 100            | 5.09           | -                      | Gao et al. (2008)           |
| Phaseolus vulgaris husk      | 180        | 1.16| 6                | 20     | 10             | 2.98           | 99.88                  | Srivastava et al. (2016)    |
| Peanut shell                 | 45         | 2   | 14.6             | 37.20  | 100            | 3.49           | 30.28                  | This work a                 |

*aExperimental conditions: [Cr (VI)] = 10–250 mg/L, adsorbent amount = 0.73 g, V = 50 mL, pH = 2.11 and contact time = 45 min at 318 K.

### Table 8 | Kinetic parameters for Cr(VI) adsorption onto PSh (experimental conditions: [Cr (VI)] = 100 mg/L, adsorbent amount = 0.73 g, V = 50 mL, pH = 2.11, and contact time = 5–120 min at 25 °C)

| Kinetic model       | Equation                                      | Parameters | Values |
|---------------------|-----------------------------------------------|------------|--------|
| Pseudo first order  | $q_t = q_e (1 - \exp (-K_1 t))$               | $q_e$ (mg/g) | 1.874  |
|                     |                                               | $K_1$ (min$^{-1}$) | 0.058  |
|                     |                                               | $R^2$      | 0.927  |
|                     |                                               | $\chi^2$   | 0.015  |
| Pseudo second order | $q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$     | $q_e$ (mg/g) | 1.986  |
|                     |                                               | $K_2$ (g/mg min) | 0.117  |
|                     |                                               | $R^2$      | 0.976  |
|                     |                                               | $\chi^2$   | 0.005  |
| Elovich model       | $q_t = \frac{1}{\beta} \ln(1 + \alpha \beta t)$ | $\alpha$ (mg/g min) | 16.244 |
|                     |                                               | $\beta$ (g/mg) | 4.769  |
|                     |                                               | $R^2$      | 0.919  |
|                     |                                               | $\chi^2$   | 0.016  |
|                     |                                               | $q_{e,\text{exp}}$ | 1.991  |
charged group on the adsorbent surface and negatively charged \( \text{CrO}_4^{2-} \) group of the chromium at low pH (Jawad et al. 2020b). Thus, electrostatic attraction plays an important role in Cr (VI) biosorption by PSh. Yi et al. (2017) proved that the adsorption of chromium on litchi peels follows the pseudo second order.

3.7. Adsorption thermodynamic study

The thermodynamic parameters were calculated using Equations (11)–(13):

\[
K_c = \frac{C_a}{C_e} \quad (11)
\]

\[
\Delta G_T = -RT \ln(K_c) \quad (12)
\]

\[
\ln(K_c) = \left( -\frac{\Delta H_T}{R} \right) \frac{1}{T} + \left( \frac{\Delta S_T}{R} \right) \quad (13)
\]

where \( \Delta G_T \) is Gibbs free energy (kJ/mol), \( \Delta S_T \) is the standard entropy (J/mol K), \( \Delta H_T \) is the standard enthalpy (kJ/mol), \( K_c \) is the thermodynamic equilibrium constant (L/g), \( R \) the universal gas constant (8.314 J/mol K), \( T \) is temperature (K), \( C_a \) and \( C_e \) are respectively the equilibrium concentrations of metal ions on the adsorbent (mg/g) and the equilibrium concentrations of metal ions in the solution (mg/L). The curve relating \( \ln(K_c) \) to \( 1/T \) (Figure 11) allows the resolve of the thermodynamic parameters presented in Table 9.

The decrease in \( \Delta G^0 \) values with an increase in temperature proves that better biosorption occurred at high temperatures (Aditya et al. 2012). Moreover, the positive value of \( \Delta H^0 \) proved that the adsorption process was endothermic (Iftekar et al. 2017). This conclusion is in agreement with the results proving the increase in Cr (VI) removal yield with temperature. In addition, the positive value of \( \Delta S^0 \) indicated an increase in the disorder between the solid and solution interface during the adsorption process. Hlihor et al. (2017) have found similar

![Figure 10](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.233/902360/wst2021233.pdf)

**Figure 10** | Plot of pseudo first order model, pseudo second order model and Elovich model for adsorption of Cr (VI) on PSh ([Cr (VI)] = 100 mg/L, adsorbent amount = 0.73 g, V = 50 mL, pH = 2.11 and contact time = 5–120 min at 25°C).

![Figure 11](http://iwaponline.com/wst/article-pdf/doi/10.2166/wst.2021.233/902360/wst2021233.pdf)

**Figure 11** | Curve \( \ln(K_c) \) versus \( 1/T \).
results saying that the adsorption of Cr (VI) on dead and living Arthrobacter viscosus biomass is endothermic due to the positive value of $\Delta H^o$. A positive value of $\Delta S^o$ reflects the affinity of biomass towards chromium ions in aqueous solution.

### 3.8. PSh reusability and Cr (VI) recovery

Desorption is required to manage the biosorbent waste to avoid the generation of secondary waste and recovery of valuable materials. As low pH (pH = 2.0) was favorable for Cr(VI) uptake, recovery of consumed PSh was performed using 0.1 M NaOH solvent as a basic desorbent, 0.1 M NaCl and deionized water as a neutral desorbents. Figure 12 showed the outcomes of the PSh biosorbent reusability. From the different regenerants studied, it was detected that NaOH provided the best regenerability outcomes for the PSh biosorbent as shown in Figure 12. The biosorbent suffered a friendly loss of <5% in chromium ions recovery efficiency till 3 recycle runs when washed with NaOH solvent. Desorption of Cr (VI) from the PSh biosorbent surface at strong basic pH environment can occur due to the exchange of CrO$_4^{2-}$ (the dominant species of Cr (VI) in alkaline solution) with hydroxyl ions (Ye et al. 2019). Daneshvar et al. was found similar results studying Cr (VI) desorption by NaOH solution at pH 12 (Daneshvar et al. 2019). They assured that attacking on adsorption sites by OH$^-$ ions led to Cr (VI) desorption. In another work, the maximum desorption efficiency of Cr(VI) was noted as 98.45% by 0.8 M NaOH solution (Akram et al. 2017). They explained that by the electrostatic repulsion, due to negatively charged sites of sorbent, increases Cr(VI) desorption from the adsorbent.

To make the desorption process more environmental friendly, desorption of Cr (VI) efficiency was also investigated using NaCl and deionized water. However, the loss in Cr (VI) removal efficiency by the regenerated biosorbent was >5% after the first recycle run. In agreement with our results, Cheng et al. found extremely low Cr(VI) efficiency desorption using deionized water (>3%) and high desorption efficiency (<84%) using NaOH solution (Cheng et al. 2011). They concluded that desorption of Cr (VI) by chemical adsorption and ion exchange mechanisms is more efficient than desorbed during washing by deionized water.

---

### Table 9 | Thermodynamic parameters

| Temperature (K) | $\ln (K_c)$ | $\Delta G_f$ (kJ/mol) | $\Delta H_f$ (kJ/mol) | $\Delta S_f$ (J/molK) |
|-----------------|-------------|----------------------|----------------------|---------------------|
| 298             | -1.031      | 2.554                | 11.749               | 30.839              |
| 308             | -0.883      | 2.262                |                      |                     |
| 318             | -0.732      | 1.937                |                      |                     |

---

**Figure 12** | Regeneration studies of the PSh biosorbent.
3. CONCLUSION

Hexavalent chromium removal from aqueous solution is a worldwide environmental concern. Studies have used diverse processes to attain a Cr(VI) free environment or achieve the stringent guidelines of governmental rules. In this study, a response surface methodology (RSM) with Central Composite Design (CCD) was used to develop mathematical model and optimize process conditions (pH, adsorbent amount and temperature) for Cr (VI) removal from wastewater by biosorption on PSh with a less number of experiments. The value of the adjusted coefficient of determination $R^2 = 0.972$ showed that the % removal of Cr (VI) predicted by the model is correlated with that found experimentally. ANOVA study shows the significance of generated models and depicts that pH has the most significant effect on response which has substantial effect on the removal efficiency of Cr (VI). Temperature and adsorbent amount have comparatively less significant effects on the response of Cr (VI) removal yield. The optimal parameters to remove Cr (VI) from aqueous solution at constant short time of 45 min and constant initial Cr (VI) concentration of 100 mg/L using PSh were found to be pH 2.11, biosorbent amount 0.73 g and temperature of 37.2 °C. At these conditions maximum chromium removal (29.49%) was achieved, which was rather near to the predicted value (30.28%) obtained from RSM model.

Peanut shells were characterized by SEM, EDX, FTIR, BET, XRD, Boehm method and pH zero charge analyses. The isotherm and kinetic data were described by Langmuir and the pseudo-second order models, while maximum adsorption capacity attributed to Langmuir model was 3.49 mg/g for 0.73 g PSh at 318 K. This biosorbent was an efficient material despite its low specific area. The thermodynamic analysis also demonstrated that the biosorption process was endothermic as did the positive heat of enthalpy $\Delta H^\circ$, accompanied by a positive value of entropy change $\Delta S^\circ$. The PSh waste biomass proved good regeneration potential, precisely with NaOH washing, up to three successive biosorption runs. The results of this study proved that the reported material is efficient to remove 30.28% from 100 mg/L of Cr (VI) from aqueous solutions. The material has advantages such as shortest sorption time, easy to use, economic, sensitive and selective for the removal of hexavalent chromium from wastewater samples.

ACKNOWLEDGEMENTS

The authors are thankful for the financial support received from Faculty of Sciences of Tunis, University of Tunis El Manar. Department of Separation Science, Lappeenranta-Lahti University of Technology (LUT) of Finland for hospitality received and for providing necessary instruments for the characterization of the materiel.

DATA AVAILABILITY STATEMENT

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

REFERENCES

Adio, S. O., Omar, M. H., Asif, M. & Saleh, T. A. 2017 Arsenic and selenium removal from water using biosynthesized nanoscale zero-valent iron: a factorial design analysis. *Process Safety and Environmental Protection* **107**, 518–527. https://doi.org/10.1016/j.psep.2017.03.004.

Aditya, G. V. V., Pujitha, B. P., Babu, N. C. & Venkateswarlu, P. 2012 Biosorption of chromium onto erythrina variegata orientalis leaf powder. *Korean Journal of Chemical Engineering* **29** (1), 64–71. https://doi.org/10.1007/s11814-011-0139-9.

Aigbe, U. O. & Osibote, O. A. 2020 A review of hexavalent chromium removal from aqueous solutions by sorption technique using nanomaterials. *Journal of Environmental Chemical Engineering* **8** (6), 104503. https://doi.org/10.1016/j.jece.2020.104503.

Akram, M., Bhatti, H. N., Iqbal, M., Noreen, S. & Sadaf, S. 2017 Biocomposite efficiency for Cr(VI) adsorption: kinetic, equilibrium and thermodynamics studies. *Journal of Environmental Chemical Engineering* **5** (1), 400–411. https://doi.org/10.1016/j.jece.2016.12.002.

Ali, A. & Saeed, K. 2015 Decontamination of Cr(VI) and Mn(II) from aqueous media by untreated and chemically treated banana peel: a comparative study. *Desalination and Water Treatment* **53** (13), 3586–3591. https://doi.org/10.1080/19443994.2013.876669.

Ali, I., Alharbi, O. M. L., ALOhman, Z. A., Al-Mohaimed, A. M. & Alwarthan, A. 2019 Modeling of fenuron pesticide adsorption on CNTs for mechanistic insight and removal in water. *Environmental Research* **170**, 389–397. https://doi.org/10.1016/j.envres.2018.12.066.

Appa, R., Mhaisalkar, V. A., Naoghare, P. K. & Lataye, D. H. 2019 Adsorption of an emerging contaminant (primidone) onto activated carbon: kinetic, equilibrium, thermodynamic, and optimization studies. *Environmental Monitoring and Assessment* **191** (4), 215. https://doi.org/10.1007/s10661-019-7302-x.
Asfaram, A., Ghaedi, M., Hajati, S., Goudarzi, A. & Dil, E. A. 2017 Screening and optimization of highly effective ultrasound-assisted simultaneous adsorption of cationic dyes onto Mn-doped Fe3O4-nanoparticle-loaded activated carbon. Ultrasonics Sonochemistry 34, 1–12.

Badr, N. B. E., Al-Qahtani, K. M. & Mahmoud, A. E. D. 2020 Factorial experimental design for optimizing selenium sorption on cyperus laevigatus biomass and Green-synthesized nano-silver. Alexandria Engineering Journal 59 (6), 5219–5229. https://doi.org/10.1016/j.aej.2020.09.051.

Banerjee, M., Basu, R. & Das, S. 2019 Cu(II) removal using Green adsorbents: kinetic modeling and plant scale-up design. Environmental Science and Pollution Research 26, 1–15. https://doi.org/10.1007/s11356-018-1930-5.

Bayuo, J., Pelig-Ba, K. B. & Abukari, M. A. 2019 Adsorptive removal of chromium(VI) from aqueous solution unto groundnut shell. Applied Water Science 9 (4), 107. https://doi.org/10.1007/s13201-019-0987-8.

Ben-Ali, S., Jaucouli, I., Souissi-Najjar, S. & Ouederni, A. 2017 Characterization and adsorption capacity of raw pomegranate peel biosorbent for copper removal. Journal of Cleaner Production 142, 3809–3821. https://doi.org/10.1016/j.jclepro.2016.10.081.

Ben Khalifa, E., Rzig, B., Hamrouni, M. & Hamrouni, B. 2019 Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent. Chemometrics and Intelligent Laboratory Systems 189, 18–26. https://doi.org/10.1016/j.chemolab.2019.03.014.

Bharath, G., Rambabu, K., Hai, A., Anwer, S., Banat, F. & Ponpandian, N. 2020 Synthesis of one-dimensional magnetite hydroxyapatite nanorods on reduced graphene oxide sheets for selective separation and controlled delivery of hemoglobin. Applied Surface Science 501, 144215. https://doi.org/10.1016/j.apsusc.2019.144215.

Čelebi, H. 2020 Recovery of detox tea wastes: usage as a lignocellulosic adsorbent in Cr(VI) adsorption. Journal of Environmental Chemical Engineering 8 (5), 104310. https://doi.org/10.1016/j.jece.2020.104310.

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-bromoalkanones. Chemical Engineering Journal 173 (1), 42–48. https://doi.org/10.1016/j.cej.2011.07.033.

Chigondo, F., Nyamunda, B. C., Sithole, S. C. & Gwatidzo, L. 2013 Removal of lead (II) and copper (II) ions from aqueous solution by baobab (Adononisia digitata) fruit shells biomass. IOSR Journal of Applied Chemistry 5 (1), 43–50.

Dai, Y., Sun, Q., Wang, W., Lu, L., Liu, M., Li, J., Yang, S., Sun, Y., Zhang, K., Xu, J., Zheng, W., Hu, Z., Yang, Y., Gao, Y., Chen, Y., Zhang, X., Gao, F. & Zhang, Y. 2018 Utilizations of agricultural waste as adsorbent for the removal of contaminants: a review. Chemosphere 211, 235–255. https://doi.org/10.1016/j.chemosphere.2018.06.179.

Daneshvar, E., Zarrinnmez, M. J., Kousha, M., Hashjini, A. M., Saratale, G. D., Maiti, A., Vilhanage, M. & Bhatnagar, A. 2019 Hexavalent chromium removal from water by microalgal-based materials: adsorption, desorption and recovery studies. Bioresource Technology 293, 122064. https://doi.org/10.1016/j.biortech.2019.122064.

de Carvalho, H. P., Huang, J., Zhao, M., Liu, G., Yang, X., Dong, L. & Liu, X. 2016 Parametric and energy consumption optimization of Basic Red 2 removal by electrocoagulation/egg shell adsorption coupling using response surface methodology in a batch system. Water Science and Technology 73 (11), 2572–2582.

Ding, T. Y., Hii, S. L. & Ong, L. 2012 Comparison of pretreatment strategies for conversion of coconut husk fiber to fermentable sugars. BioResources 7 (2), 1540–1547.

Fakhri, A. 2014 Application of response surface methodology to optimize the process variables for fluoride ion removal using maghemite nanoparticles. Journal of Saudi Chemical Society 18 (4), 340–347. https://doi.org/10.1016/j.jscs.2013.10.010.

Fan, S., Wang, Y., Li, Y., Tang, J., Wang, Z., Tang, J., Li, X. & Hu, K. 2017 Facile synthesis of tea waste/Fe3O4 nanocomposite as hexavalent chromium removal from aqueous solution. RSC Advances 7 (13), 7576–7590. https://doi.org/10.1039/C6RA27781K.

Gao, H., Liu, Y., Zeng, G., Xu, W., Li, T. & Xia, W. 2008 Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste – rice straw. Journal of Hazardous Materials 150 (2), 446–452. https://doi.org/10.1016/j.jhazmat.2007.04.126.

Ge, S., Wu, Y., Peng, W., Xia, C., Mei, C., Cai, L., Shi, S. Q., Sonne, C., Lam, S. S. & Tsang, Y. F. 2020 High-pressure CO2 hydrothermal pretreatment of peanuts shells for enzymatic hydrolysis conversion into glucose. Chemical Engineering Journal 385, 123494. https://doi.org/10.1016/j.cej.2019.123494.

Gebrehawaria, G., Hussen, A. & Rao, V. M. 2015 Removal of hexavalent chromium from aqueous solutions using barks of Acacia albida and leaves of Euclia schimperi. International Journal of Environmental Science and Technology 12 (5), 1569–1580. https://doi.org/10.1007/s13762-014-0530-2.

Hamdan, S. S. & El-Naas, M. H. 2014 Characterization of the removal of Chromium(VI) from groundwater by electrocoagulation. Journal of Industrial and Engineering Chemistry 20 (5), 2775–2781. https://doi.org/10.1016/j.jiec.2013.11.006.

Hamilton, E. M., Young, S. D., Bailey, E. H. & Watts, M. J. 2018 Chromium speciation in foodstuffs: a review. Food Chemistry 250, 105–112. https://doi.org/10.1016/j.foodchem.2018.01.016.

Harbi, S., Guesmi, F., Tabassi, D., Hannachi, C. & Hamrouni, B. 2016 Application of response surface methodology and artificial neural network: modeling and optimization of Cr(VI) adsorption process using Dowex 1X8 anion exchange resin. Water Science and Technology 75 (10), 2402–2412. https://doi.org/10.2166/wst.2016.091.

Haroon, H., Ashfaq, T., Gardazi, S. M. H., Sherazi, T. A., Ali, M., Rashid, N. & Bilal, M. 2016 Equilibrium kinetic and thermodynamic studies of Cr(VI) adsorption onto a novel adsorbent of Eucalyptus camaldulensis waste: batch and column reactors. Korean Journal of Chemical Engineering 33 (10), 2898–2907. https://doi.org/10.1007/s11814-016-0160-0.
produced from Date Press Cake; an agro-industrial waste. Bioresource Technology 258, 48–56. https://doi.org/10.1016/j.biortech.2018.02.106.

Omorgie, M. O., Babalola, J. O., Unuabonah, E. I., Song, W. & Gong, J. R. 2016 Efficient chromium abstraction from aqueous solution using a low-cost biosorbent: nauclea diderrichii seed biomass waste. Journal of Saudi Chemical Society 20 (1), 49–57. https://doi.org/10.1016/j.jscs.2012.09.017.

Pakade, V. E., Tavengwa, N. T. & Madikizela, L. M. 2019 Recent advances in hexavalent chromium removal from aqueous solutions by adsorptive methods. RSC Advances 9 (45), 26142–26164. https://doi.org/10.1039/C9RA05188K.

Perea-Moreno, M.-Á., Manzano-Agugliaro, F., Hernández- Escobedo, Q. & Perea, A. 2018 Peanut shell for energy: properties and its potential to respect the environment. Sustainability 10, 3254. https://doi.org/10.3390/su10093254.

Ponnusamy, S. K. & Yashwanthraj, M. 2017 Sequestration of toxic Cr(VI) ions from industrial wastewater using waste biomass: a review. DESALINATION AND WATER TREATMENT 68, 245–266. https://doi.org/10.5004/dwt.2017.20322.

Pradhan, D., Sukla, L. B., Sawyer, M. & Rahman, P. K. S. M. 2017 Recent bioreduction of hexavalent chromium in wastewater treatment: a review. Journal of Industrial and Engineering Chemistry 55, 1–20. https://doi.org/10.1016/j.jiec.2017.06.040.

Prithvirajan, R., Jayabal, S., Sundaram, S. K. & Sangeetha, V. 2016 Hybrid biocomposites from agricultural residues: mechanical, water absorption and tribological behaviors. Journal of Polymer Engineering 36 (7), 663–671. https://doi.org/10.1515/polyeng-2015-0113.

Rambabu, K., Bharath, G., Banat, F. & Show, P. L. 2020 Biosorption performance of date palm empty fruit bunch wastes for toxic hexavalent chromium removal. Environmental Research 187, 109694. https://doi.org/10.1016/j.envres.2020.109694.

Rangabhishayim, S., Sayantani, S. & Balasubramanian, P. 2019 Assessment of hexavalent chromium biosorption using biodiesel extracted seeds of Jatropha sp., Ricinus sp. And Pongamia sp. International Journal of Environmental Science and Technology 16 (10), 5707–5724. https://doi.org/10.1007/s13762-018-1951-0.

Raza, M. H., Sadiq, A., Farooq, U., Athar, M., Hussain, T., Mujahid, A. & Salman, M. 2015 Phragmites karka as a biosorbent for the removal of mercury metal ions from aqueous solution: effect of modification. Journal of Chemistry 2015, 1–12. https://doi.org/10.1155/2015/293054.

Rosales, E., Escudero, S., Pazos, M. & Sanromán, M. A. 2019 Sustainable removal of Cr(VI) by lime peel and pineapple core wastes. Applied Sciences 9 (10), 1967. https://doi.org/10.3390/app9101967.

Sareena, C., Sreejith, M. P., Ramesan, M. T. & Purushothaman, E. 2014 Biodegradation behaviour of natural rubber composites reinforced with natural resource fillers – monitoring by soil burial test. Journal of Reinforced Plastics and Composites 33, 416–433. https://doi.org/10.1177/0743284413519594.

Sharma, P. K., Ayub, S. & Tripathi, C. N. 2016 Isotherms describing physical adsorption of Cr(VI) from aqueous solution using various agricultural wastes as adsorbents. Cogent Engineering 3 (1), https://doi.org/10.1080/23316916.2016.1168657.

Sorita, G. D., Leizmann, F. V. & Salvador Ferreira, S. R. 2020 Biorefinery approach: is it an upgrade opportunity for peanut by-products? Trends in Food Science & Technology 9092422420305689. https://doi.org/10.1016/j.tifs.2020.08.011.

Srivastava, S., Agrawal, S. B. & Mondal, M. K. 2016 Characterization, isotherm and kinetic study of Phaseolus vulgaris husk as an innovative adsorbent for Cr(VI) removal. Korean Journal of Chemical Engineering 33 (2), 567–575. https://doi.org/10.1007/s11814-015-0165-0.

Sun, J., Chang, S., Li, R. & Huang, J. 2007 Factors affecting co-removal of chromium through copper precipitation. Separation and Purification Technology 56 (1), 57–62. https://doi.org/10.1016/j.seppur.2007.01.013.

Surip, S. N., Abdulhameed, A. S., Garba, Z. N., Syed-Hassan, S. S. A., Ismail, K. & Jawad, A. H. 2020 H2SO4-treated Malaysian low rank coal for methylene blue dye decolourization and COD reduction: optimization of adsorption and mechanism study. Surfaces and Interfaces 21, 100641. https://doi.org/10.1016/j.surif.2020.100641.

Tadesse, B., Teju, E. & Megersa, N. 2014 The Teff straw: a novel low-cost adsorbent for quantitative removal of Cr(VI) from contaminated aqueous samples. Desalination and Water Treatment 1–12. https://doi.org/10.1080/19443994.2014.968214.

Taşar, Ş., Kaya, F. & Özer, A. 2014 Biosorption of lead(II) ions from aqueous solution by peanut shells: equilibrium, thermodynamic and kinetic studies. Journal of Environmental Chemical Engineering 2 (2), 1018–1026. https://doi.org/10.1016/j.jece.2014.05.015.

Thommes, M., Kaneko, K., Neimark, A. V., Olivier, J. P., Rodriguez-Reinoso, F., Rouquerol, J. & Sing, K. S. 2015 Physiosorption of metals, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). Pure and Applied Chemistry 87 (9–10), 1051–1069.

Touihri, M., Guesmi, F., Hannachi, C., Harmouni, B., Sellaoui, L., Badawi, M., Poch, J. & Fioli, N. 2021 Single and simultaneous adsorption of Cr(VI) and Cu (II) on a novel Fe3O4/pine cones gel beads nanocomposite: experiments, characterization and isotherms modeling. Chemical Engineering Journal 416, 129101. https://doi.org/10.1016/j.cej.2021.129101.

Valentín-Reyes, J., García-Reyes, R. B., García-González, A., Soto-Regalado, E. & Cerino-Cordova, F. 2019 Adsorption mechanisms of hexavalent chromium from aqueous solutions on modified activated carbons. Journal of Environmental Management 256, 815–822. https://doi.org/10.1016/j.jenvman.2019.02.014.

Wang, Q., Zhou, C., Kuang, Y., Jiang, Z. & Yang, M. 2020 Removal of hexavalent chromium in aquatic solutions by pomelo peel. Water Science and Engineering 15 (1), 65–73. https://doi.org/10.1016/j.wse.2019.12.011.

Ye, Z., Yin, X., Chen, L., He, X., Lin, Z., Liu, C., Ning, S., Wang, X. & Wei, Y. 2019 Integrated process for removal and recovery of Cr(VI) from electroplating wastewater by ion exchange and reduction–precipitation based on a silica-supported pyridine resin. Journal of Cleaner Production. Available from: https://agnis.fao.org/agnis-search/search.do?recordID=US202000034681.
Yi, Y., Lv, J., Liu, Y. & Wu, G. 2017 Synthesis and application of modified Litchi peel for removal of hexavalent chromium from aqueous solutions. *Journal of Molecular Liquids* **225**, 28–33. https://doi.org/10.1016/j.molliq.2016.10.140.

Zhao, B., Ren, L., Du, Y. & Wang, J. 2020 Eco-friendly separation layers based on waste peanut shell for gravity-driven water-in-oil emulsion separation. *Journal of Cleaner Production* **255**, 120184. https://doi.org/10.1016/j.jclepro.2020.120184.

Zhu, C.-S., Wang, L.-P. & Chen, W. 2009 Removal of Cu(II) from aqueous solution by agricultural by-product: peanut hull. *Journal of Hazardous Materials* **168** (2–3), 739–746. https://doi.org/10.1016/j.jhazmat.2009.02.085.

First received 25 January 2021; accepted in revised form 8 June 2021. Available online 18 June 2021.