Selective Removal of Hexavalent Chromium from Wastewater by Rice Husk: Kinetic, Isotherm and Spectroscopic Investigation

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Abstract: Chromium (Cr) in water bodies is considered as a major environmental issue around the world. In the present study, aqueous Cr(VI) adsorption onto rice husk was studied as a function of various environmental parameters. Equilibrium time was achieved in 2 h and maximum Cr(VI) adsorption was 78.6% at pH 5.2 and 120 mg L\(^{-1}\) initial Cr(VI) concentration. In isotherm experiments, the maximum sorption was observed as 379.63 mg g\(^{-1}\). Among four isotherm models, Dubinin–Radushkevich and Langmuir models showed the best fitting to the adsorption data, suggesting physical and monolayer adsorption to be the dominant mechanism. The kinetic modeling showed that a pseudo-second order model was suitable to describe kinetic equilibrium data, suggesting a fast adsorption rate of Cr(VI). The results of FTIR spectroscopy indicated that mainly –OH and C–H contributed to Cr(VI) adsorption onto rice husk. This paper provided evidence that rice husk could be a cost-effective, environment-friendly and efficient adsorptive material for Cr(VI) removal from wastewater due to its high adsorption capacity.

Keywords: chromium; functional groups; isotherm; rice husk

1. Introduction

Aquatic systems have been contaminated by the addition of heavy metals over the past few decades. Major heavy metals of concern in water bodies are zinc (Zn), chromium (Cr), lead (Pb), silver (Ag), nickel (Ni) and copper (Cu) [1]. Industrial sources, combustion by-products, smelters and foundries, automobiles and the paint industry are major sources of heavy metals contamination in aqueous systems. In the natural environment, the release of toxic heavy metals, for example, irrigation of agricultural land with sewage, allows non-biodegradable and persistent heavy metals to enter into the food chain [2,3].

Contamination of water with Cr, specifically hexavalent Cr (Cr(VI)), is a major problem for the environment and humans, considering its toxicity and disease-causing effects. Chromium occurs as ores and in various compound forms in the earth’s crust. The sources of Cr contamination of water bodies include the disposal of industrial effluents from leather tanning, electroplating, metal finishing, pigments, dyes, paints and ceramics industries [2,4]. Chromium exists in two stable oxidation forms in the natural environment: Cr(VI) and trivalent Cr (Cr(III)). Cr(III) is less toxic and can be used as a micronutrient for the human body [5]. In contrast, Cr(VI) is an extremely stable, mobile and toxic species with relatively higher solubility in water than Cr(III). The toxicity of Cr(VI) is about 500 times higher.
as compared to Cr(III), thus Cr(VI) has been classified as Class-I human carcinogen [6]. According to the USEPA, 0.05 mg L\(^{-1}\) is the maximum contamination level (MCL) of Cr(VI) in domestic water supplies [5]. Therefore, high Cr(VI) concentrations in water should be decreased below the MCL before discharging.

Various techniques, such as precipitation, solvent extraction, flotation, evaporation, reverse osmosis and ion exchange, have been introduced to deal with Cr(VI) originating from industrial effluents and wastewater [7,8]. However, these conventional methods have proved to be expensive and impractical due to higher capital cost and energy requirement [9–11]. In the recent past, adsorption has emerged as an inexpensive and efficient method for the removal of Cr(VI) from contaminated water. In previous studies different commercial adsorbents and agricultural residues, such as tea waste, turmeric waste, Jatropha curcus, citrus peel, water melon peel, coconut husk, wheat straw and bamboo, etc., were used as adsorbents for the removal of Cr(VI) and other heavy metals from contaminated water [12–14].

In Asia, including Pakistan, rice-producing countries are producing rice husk as an agricultural waste material. Approximately 500 million metric tons is the annual rice production worldwide, of which 10%–20% is rice husk [15]. About 70%–85% organic matter exists in rice husk, which contains sugars, cellulose and lignin, etc., while silica is also present in the cellular membrane [16]. Rice husk could be a good material for the removal of Cr(VI) from contaminated water because different surface functional groups, including hydroxyl and carboxyl groups, are present on the surface of rice husk [17,18]. Although literature is available in which rice husk was used for the removal of aqueous Cr(VI), more work is required to reveal the optimum environmental conditions, such as a relatively higher pH (close to natural water) for maximum efficiency. Moreover, to our knowledge, in Pakistan limited/no data exists in which rice husk was used as an adsorbent for Cr(VI) removal from wastewater, particularly in the presence of co-occurring ions such as sulfate, phosphate and nitrate. Thus, the potential aim of this study was the elimination of Cr(VI) from contaminated water by applying rice husk as an adsorbent. The effect of various environmental parameters, such as pH, sorbent dose, initial metal concentration, contact time and co-occurring ions, was studied. Finally, the mechanism involved in the adsorption of Cr(VI) from wastewater by rice husk was revealed using isotherm and kinetic modeling as well as the FTIR spectroscopy technique.

2. Materials and Methods
2.1. Experimental Chemicals and Analysis

A stock solution of Cr(VI) (up to 4000 mg L\(^{-1}\)) for a batch adsorption system was prepared by adding a defined quantity of K\(_2\)Cr\(_2\)O\(_7\) to deionized water (DW). Glassware and plasticware were washed completely with DW followed by soaking in 3% HNO\(_3\) solution. The study was carried out in triplicates. The Cr(VI) concentration in sorption solutions was determined using an atomic absorption spectrometer (AAS) (Model, Nova 350, Analytik Jena).

2.2. Biosorbent Material Collection and Preparation

The material (rice husk) for biosorbent preparation was collected from a rice mill. It was sun-dried and oven-dried (65 °C) for 2 and 3 days, respectively. The material was ground thoroughly after drying and sieved (size < 250 µm).

2.3. Chromium Adsorption Using Batch System

Experiments were conducted in 50 mL falcon plastic vials, and NaCl solution having 0.01 M concentration was employed as a background working solution. The shaking time and experimental temperature were applied as 2 h and 20 ± 2 °C, respectively, during adsorption studies. Specifically, to check the pH effect spanning 3 to 10, 25 mL working solution was prepared with Cr(VI) concentration of 120 mg L\(^{-1}\) and 0.6 g L\(^{-1}\) rice husk dosage. The required pH for each working solution was adjusted using either (0.01 M) HCl solution or (0.01 M) NaOH solution. The working solutions were agitated for 2 h followed
by centrifugation and filtration. The remaining concentration of Cr(VI) was estimated using AAS as described above.

To conduct the isotherm study, initial concentrations of Cr(VI) were varied from 10 to 250 mg L\(^{-1}\) with 2 h of shaking time and rice husk dosage of 0.6 g L\(^{-1}\). The pH in the experiment was maintained at 5.2 (found from pH experiments). The remaining concentration of Cr(VI) was estimated using AAS as described above.

The influence of sorbent dosage was determined using a defined amount of rice husk spanning 0.1 to 1.3 g L\(^{-1}\); i.e., 0.1, 0.3, 0.6, 0.9, 1.1, 1.3 g L\(^{-1}\). The adsorption solution pH was set at 5.2 while the applied Cr(VI) concentration was 120 mg L\(^{-1}\). The mixture was agitated for 2 h followed by centrifugation and careful filtration. The remaining Cr(VI) in the samples was analyzed on AAS.

In the kinetic study, 5.2 pH level, 120 mg L\(^{-1}\) Cr(VI) concentration and 0.6 g L\(^{-1}\) rice husk dosage were used. The sorption solution mixture was agitated for contact time spanning 0.016 to 24 h. The remaining Cr(VI) in the samples was analyzed on AAS.

In order to check the influence of co-occurring ions (sulfate, nitrate and phosphate) in the water, 50 mg L\(^{-1}\) of each ion (sulfate, nitrate and phosphate) was added to the sorption working solution. The remaining Cr(VI) in the sorption solution was estimated on AAS.

The removal rate of Cr(VI) by rice husk was computed as follows (Equation (1)):

\[
\% \text{ Cr removal} = \frac{C_o - C_e}{C_o} \times 100
\]

The \(q_e\), Cr(VI) adsorbed (mg g\(^{-1}\)) was obtained as shown in Equation (2):

\[
q_e = \frac{(C_o - C_e)V}{m}
\]

In both the equations, equilibrium Cr(VI) concentration (mg L\(^{-1}\)), initial Cr(VI) concentration (mg L\(^{-1}\)), volume of working solution (L), and biomass of rice husk (g) are illustrated by \(C_e\), \(C_o\), \(V\) and \(m\), respectively.

### 2.4. Modeling and Statistical Analysis

The modeling of data obtained from kinetic and isotherm experiments was carried out using Microsoft\textsuperscript{®} Excel 2010 and Sigma Plot version 10 [12].

### 2.5. Analyses of Rice Husk Using FTIR Spectroscopy

The functional groups present on the rice husk surface were identified by collecting the FTIR spectra (TENSOR-II, Bruker, Ettlingen, Germany) spanning 400–4000 cm\(^{-1}\) wavenumber.

### 3. Results and Discussion

#### 3.1. Influence of Varying pH Levels

The pH of the sorption working solution is a very important parameter during the adsorption process. The solution pH can have a direct effect by influencing the physicochemical features (diffusion process, surface charge, surface binding and speciation of metals) of both adsorbate and adsorbent [19,20]. Variations in pH could alter speciation of heavy metals and the surface charge of adsorbents.

Rice husk as sorbent was analyzed with respect to different values of pH levels during Cr(VI) sorption. The results showed that the adsorbent’s (rice husk’s) capacity to remove the specific quantity of Cr(VI) was dependent upon the pH value of the solution. Figure 1a shows that from pH value 3 to 5.2, the Cr(VI) sorption percentage was increased and reached at maximum value of 78.6% (Table S1). At a relatively low pH value (5.2), the hydroxyl (OH\(^{-}\)) ions having negative charge were neutralized with excess H\(^{+}\) ions (positive charges) and the adsorption onto rice husk succeeded by enabling the diffusion of dichromate ions.
The species of Cr(VI) exists as HCrO₄⁻, HCr₂O₇⁻, H₂CrO₄ (pH < 1), Cr₂O₇²⁻ and CrO₄²⁻ (pH 2–6) depending upon the pH of the solution, thus the pH could play a major role in metal ions’ sorption onto biosorbents [21]. In this study, an increase in pH of the solution caused transformation of HCrO₄⁻ to CrO₄²⁻ and Cr₂O₇²⁻, which could be due to the considerable interaction of negatively charged ions of Cr(VI) with positive charges from the biosorbent. Sorption of Cr(VI) declined with the additional rise in the solution pH value (>5.2) due to the existence of hydroxyl ions (OH⁻) in a higher amount at increased pH and thus biosorbent capacity decreased. Moreover, the surface of the adsorbent becomes negatively charged with the presence of a higher amount of OH⁻ ions, thus decreasing Cr(VI) ions’ diffusion, which results in the production of negative repulsive forces between the biosorbent and Cr(VI) ions [16,19,20].

3.2. Contact Time

The optimum sorption solution agitation time was determined for better performance of rice husk in removing Cr(VI). Figure 1b,c describes the contact time study for the percentage removal and average uptake of Cr(VI) by rice husk.

Figure 1b shows the ability of rice husk in mg g⁻¹ for successful removal of Cr(VI) with a range of contact times. It was observed that the rice husk’s adsorption capacity was 192.82 mg g⁻¹ at 1 h agitation time and improved a little (193.42 mg g⁻¹) when equilibrium was obtained at 2 h agitation time and became almost constant afterwards (Table S2). To reach equilibrium, sorption kinetics have two phases, a rapid stage and slower stage [20,22–24]. At the beginning, adsorption was very fast and removal percentage of Cr(VI) increased quickly for 1 h. The percentage of Cr(VI) removed by rice husk reached
93.60% in 1 h and, after achieving equilibrium at 2 h contact time, the removal of Cr(VI) increased slightly further (93.89%) as shown in Figure 1c.

The increasing contact time after 2 h had a negligible effect on Cr(VI) adsorption. At contact time of 2 h, the maximum Cr(VI) removal obtained showed that in the sorption process the Cr(VI) uptake capacity of rice husk was more at the beginning of the adsorption process owing to availability of abundant cavities for capturing Cr(VI) ions. Moreover, at the start, the excess of active binding sites enhanced the rate of sorption, which was decreased with increasing agitation time (<2 h) due to fraction surface lessening and strong competition among Cr(VI) ions for adsorption sites [12,25,26].

Ali et al. [27] also observed that the maximum sorption percentage removal of Cr(VI) was achieved at 100 and 120 min contact time, while no further increase in Cr(VI) removal was detected with the rise in contact time.

3.3. Initial Chromium Concentration

The initial concentration of sorbate is also a critical parameter since it produces a driving force which transfers the sorbate ions onto the biosorbent from liquid solution [19].

Different Cr(VI) ion concentrations spanning from 10 to 250 mg L\(^{-1}\) were used for this study. Figure 1d shows that the sorption capacity of rice husk was enhanced from 24.31 to 351.92 mg g\(^{-1}\) with rising Cr(VI) level from 10 to 120 mg L\(^{-1}\) (Table S3). When the initial concentration of Cr(VI) reached 40 mg L\(^{-1}\), the rise in adsorption rate became relatively slow, even at the equilibrium level of 120 mg L\(^{-1}\) [19].

The Cr(VI) ions’ sorption was at a minimum when the Cr(VI) level was low but a significant sorptive reaction among sorption sites and Cr(VI) ions was favored by the increase in Cr(VI) level until equilibrium was reached at 120 mg L\(^{-1}\) [28]. Afterwards, increasing the initial Cr(VI) level had negligible effect on Cr(VI) adsorption by rice husk.

3.4. Sorbent Dosage

The sorbent dose effect was investigated with 120 mg L\(^{-1}\) initial concentration of Cr(VI), 5.2 solution pH and 2 h contact time with 0.1 to 1.3 g L\(^{-1}\) rice husk dose. Results showed that with the rising dosage of rice husk, the removal rate of Cr(VI) was increased from 60.07% to 69.18% as shown in Figure 1e and Table S4. Due to the increase in rice husk dose (up to 0.6 g L\(^{-1}\)), higher surface area and exchangeable sites were available for Cr(VI) but the Cr(VI) percentage elimination was decreased considerably from 65.75% to 55.65% as the rice husk dosage was increased from 0.9 to 1.3 g L\(^{-1}\). This reduction in Cr(VI) removal could be because of the overcrowding/overlapping of biosorbent particles, thus reducing the number of binding sites for Cr(VI) ions [29,30].

3.5. Co-occurring Ions

Industrial wastewater contains many other anions such as NO\(_3\)^\(^-\), PO\(_4\)^\(_{3-}\) and SO\(_4\)^\(_{2-}\) and sorption of Cr(VI) could be disturbed in the presence of these anions. Figure 2 shows the co-occurring ions’ effect on sorption of Cr(VI) in water: it was found that the occurrence of PO\(_4\)^\(_{3-}\), NO\(_3\)^\(^-\) and SO\(_4\)^\(_{2-}\) seriously affected the Cr(VI) sorption by rice husk.

During the Cr adsorption study with rice husk, the greatest decline in Cr(VI) sorption percentage (60.12%) was owing to the co-existence of SO\(_4\)^\(_{2-}\) ions. NO\(_3\)^\(^-\) and PO\(_4\)^\(_{3-}\) ions’ presence also showed reduction in the percentage Cr(VI) removal to 72.01% and 68.5%, respectively, but the Cr(VI) sorption in the existence of PO\(_4\)^\(_{3-}\) and NO\(_3\)^\(^-\) was higher as compared to SO\(_4\)^\(_{2-}\). From the results, it can be concluded that the sorption potential of rice husk was significantly affected when SO\(_4\)^\(_{2-}\) ions were present compared to NO\(_3\)^\(^-\) and PO\(_4\)^\(_{3-}\) ions.
3.6. Sorption Kinetic Modeling

Various mathematical models could evaluate the biosorption kinetics. Under various experimental conditions, the batch sorption behavior could be explained clearly by a kinetics model [31,32]. Thus, to determine the rate of biosorption in a batch system, the kinetics models pseudo-first order (PFO) and pseudo-second order (PSO) were applied. Figure 3 demonstrates PFO and PSO for rice husk as a sorbent while Table 1 represents the constant rate (k1, k2), regression coefficients ($R^2$) and $q_e$ values of rice husk as a biosorbent. It was observed that the PSO model showed a better fit to experimental kinetic results compared to PFO. The results of modeling showed that the $R^2$ value of PSO (0.99) was higher than that of PFO (0.75) and the $q_e$ of PSO was also close to the experimental data. Considering the sorption mechanism, Cr(VI) sorption by rice husk was due to the chemisorption process as PSO was a more appropriate fit to the kinetic equilibrium data [19].

![Figure 2](image1.png)

**Figure 2.** The Cr(VI) adsorption (%) in the occurrence of competing ions.

![Figure 3](image2.png)

**Figure 3.** Kinetic modeling with (a) pseudo-first order (PFO) and (b) pseudo-second order (PSO) data for Cr(VI) adsorption onto rice husk.
Table 1. Parameters of kinetic modeling for Cr(VI) elimination by rice husk.

|                  | Pseudo-First Order | Pseudo-Second Order |
|------------------|-------------------|---------------------|
| $k_1$ (min$^{-1}$) | 0.02              | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.005 |

3.7. Sorption Isotherm Modeling

Four non-linear isotherms were employed to delineate the Cr(VI) adsorption onto rice husk as shown in Figure 4 and Table 2.

The $Q_L$ value obtained from the Langmuir model was observed to be 33.68 mg g$^{-1}$ for Cr(VI) adsorption onto rice husk. The Langmuir model fitting demonstrated that the Cr(VI) sorption by rice husk from wastewater was mainly owing to monolayer sorption, which was controlled by chemisorption [17]. The separation factor ($R_L$) demonstrated that Cr(VI) sorption by rice husk is a highly favorable reaction ($R_L \leq 1$), as shown in Figure 4b.

The Freundlich isotherm model showed that $R^2$ and $Q_F$ values were 0.70 and 99.5 mg$^{1-n}$ g$^{-1}$ L$n$ while the Temkin model demonstrated that the $R^2$ value was 0.77 for Cr(VI) sorption onto rice husk. Lower heat of sorption (b) was observed with the Temkin model for Cr(VI) sorption, which indicates that a linear decrease in (b) value established a superior coverage of Cr(VI) on the rice husk surface, as shown in Table 2.
Table 2. Parameters of isotherm modeling for Cr(VI) elimination by rice husk.

| Isotherm Model       | Parameters Obtained Value |
|----------------------|---------------------------|
| Langmuir             | \( Q_L \) (mg g\(^{-1}\)) | 33.68 |
|                      | \( R^2 \)                 | 0.84  |
|                      | \( K_L \) (L g\(^{-1}\))  | 0.08  |
| Freundlich           | \( Q_F \) (mg\(^{1-n}\) \(g\(^{-1}\) L\(^n\)) | 99.5  |
|                      | \( R^2 \)                 | 0.70  |
|                      | \( n \)                   | 0.25  |
| Temkin               | \( b \)                   | 1.04  |
|                      | \( R^2 \)                 | 0.77  |
|                      | \( A \)                   | 73.28 |
| Dubinin–Redushkevich| \( Q_D \) (mg g\(^{-1}\)) | 371.73|
|                      | \( R^2 \)                 | 0.93  |
|                      | \( E \) (kJ g\(^{-1}\))  | 0.02  |

The Dubinin–Radushkevich model fit for Cr(VI) sorption is shown in Figure 4a. The Dubinin–Radushkevich model showed a higher \( R^2 \) value for rice husk. In Dubinin–Redushkevich model bonding, energy \( (E) \) was calculated to clarify the Cr(VI) adsorption onto rice husk (Table 2). The sorption process is physical if \( E < 8 \text{ kJ g}^{-1} \); it might be illustrated by diffusion mechanism if \( E > 16 \text{ kJ g}^{-1} \) or chemisorption when \( E = 8–16 \text{ kJ g}^{-1} \). In the current study, the value of \( E \) was 0.02 kJ g\(^{-1}\), hence the dominant mechanism could be physical sorption [32]. It can be deduced from the isotherm results that Cr(VI) adsorption onto rice husk was mainly due to physical sorption and the monolayer sorption process. It was found that the best fitting model was the Dubinin–Radushkevich model followed by the Langmuir model compared to the other two models for Cr(VI) adsorption by rice husk, as indicated by higher \( R^2 \) values (0.93 and 0.84, respectively).

3.8. Cr (VI) Biosorption Mechanism through FTIR Spectroscopy

Surface functional groups involved in Cr(VI) sorption onto the biosorbent surface were quantitatively analyzed, and for this purpose FTIR spectra of Cr(VI) loaded and unloaded biosorbent were obtained. Figure 5 describes the FTIR spectra of rice husk (a) no Cr and (b) Cr adsorbed.

In Figure 5, the peaks at 3354 and 3377 cm\(^{-1}\) of natural rice husk and Cr(VI) adsorbed rice husk, respectively, indicated the –OH stretching vibrations with the association of macromolecules (pectin, lignin and cellulose) [33–35]. The C-H bands were recorded at 2880 and 2884 cm\(^{-1}\) of natural rice husk and Cr(VI)-adsorbed rice husk, respectively, which might be due to the methoxy, methyl and methylene functional groups [36]. The absorption peaks at 1280, 1508 and 1682 cm\(^{-1}\) of natural rice husk whereas peaks at 1295, 1541 and 1683 cm\(^{-1}\) of Cr(VI)-adsorbed rice husk showed the involvement of ionic carboxylic groups (COO–). There were bands at 706 and 777 cm\(^{-1}\) of natural rice husk whereas those at 738 and 835 cm\(^{-1}\) of Cr(VI) rice husk were due to the vibrations of the –NH\(_2\) group [29].

The FTIR spectral peaks of natural rice husk at 3354, 2880, 1651, 1507, 1280, 777 and 706 cm\(^{-1}\) were shifted to the peaks 3377, 2884, 1685, 1541, 1295, 835 and 738 cm\(^{-1}\) after loading of Cr(VI). The changes in spectral bands’ positions might be ascribed to the Cr(VI) sorption owing to involvement of functional groups on the biosorbent surface through the ion exchange mechanism [37]. Results showed that functional groups –OH and C-H were mainly involved in the process of sorption with highest peaks, while the other functional groups, such as COO– and –NH\(_2\), were also involved with low peaks. The same responses with almond shell and apricot shell were recorded previously regarding the sorption of Cr(VI) [38]. Rice straw, rice bran and sawdust were also observed as a biosorbent for sorption of Cr(VI), and similar results of functional group analyses were noted [39].
Figure 5. The FTIR spectra of rice husk (a) no Cr(VI); (b) Cr(VI)-adsorbed.

Table 3 compares the adsorption capacities of rice husk used in this study with those in other studies. It can be observed from Table 3 that rice husk showed relatively higher Cr(VI) adsorption potential compared to biosorbents previously used by several researchers.
Table 3. Comparison of various biosorbents with rice husk for Cr(VI) adsorption.

| Biosorbent                 | Adsorption (mg g$^{-1}$) | References          |
|----------------------------|--------------------------|---------------------|
| Litchi peel                | 7.05                     | Yi et al. [40]      |
| Foxtail millet shell       | 11.70                    | Peng et al. [41]    |
| Grapefruit peels           | 39.06                    | Rosales et al. [42] |
| Freshwater snail shell     | 8.85                     | Vu et al. [43]      |
| Pomegranate seeds          | 3.32                     | Ghaneian et al. [44]|
| Bamboo shoot shell         | 28.72                    | Hu et al. [45]      |
| Rose biomass               | 5.26                     | Aman et al. [46]    |
| Waste Chlorella vulgaris   | 43.3                     | Xie et al. [47]     |
| Rice husk                  | 351.92                   | This study          |

4. Conclusions

Rice husk was used successfully for Cr(VI) biosorption from contaminated water streams. The results showed that rice husk removed 78.6% Cr(VI) from the wastewater and the highest Cr(VI) elimination was found at 5.2 pH. The data obtained from various studied parameters showed that 2 h contact time, 120 mg L$^{-1}$ initial metal concentration and 0.6 g L$^{-1}$ rice husk dosage were perfect for efficient adsorption of Cr(VI) from polluted water. Dubinin–Radushkevich and Langmuir models provided the best fit to the equilibrium data indication that the Cr(VI) onto rice husk was due to physical and monolayer sorption processes. The pseudo-second order model fitting proposed that adsorption of Cr(VI) was a fast process. The data from the effect of co-occurring ions showed that the presence of sulfate ions during sorption of Cr(VI) reduced the rice husk’s capacity for Cr(VI) adsorption. The FTIR analysis suggested that –NH$_2$, alkyl, –OH and COO– functional groups were the main species involved in Cr(VI) removal. Overall, since rice husk used here was an agricultural waste which is inexpensive, accessible and proved to be an effective sorbent, therefore, this prepared biosorbent is expected to be economically feasible for the treatment of Cr(VI)-containing wastewater.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4414/13/3/263/s1, Table S1: Effect of solution pH on Cr adsorption by rice husk; Table S2: Effect of contact time on Cr adsorption by rice husk; Table S3: Effect of initial Cr concentration on Cr adsorption by rice husk; Table S4: Effect of sorbent dose on Cr adsorption by rice husk.

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References

1. Ahalya, N.; Kanamadi, R.D.; Ramachandra, T.V. Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (Cicer arietinum). *Electr. J. Biotechnol.* 2005, 8, 258–264. [CrossRef]

2. Dhanakumar, S.; Solaraj, G.; Mohanraj, R.; Pattabhi, S. Removal of Cr (VI) from aqueous solution by adsorption using cooked tea dust. *Ind. J. Sci. Technol.* 2007, 1, 1–6. [CrossRef]

3. Mahvi, A.H.; Naghipour, D.; Vaeei, F.; Nazmara, S. Teawaste as an adsorbent for heavy metal removal from industrial wastewaters. *Am. J. Appl. Sci.* 2005, 2, 372–375. [CrossRef]

4. Gopalakrishnan, S.; Kannadasan, T.; Velmurugan, S.; Muthu, S.; Vinoth Kumar, P. Biosorption of chromium (VI) from industrial effluent using neem leaf adsorbent. *Res. J. Chem. Sci.* 2013, 3, 48–53.

5. Monnot, A.D.; Christian, W.V.; Paustenbach, D.J.; Finley, B.L. Correlation of blood Cr(III) and adverse health effects: Application of PBPK modeling to determine non-toxic blood concentrations. *Crit. Rev. Toxicol.* 2014, 44, 618–637. [CrossRef]

6. Levankumar, L.; Uthukumaran, V.; Gobinath, M. Batch adsorption and kinetics of chromium(VI) removal from aqueous solutions by *Ocimum americanum* L. seed pods. *J. Hazard. Mater.* 2009, 161, 709–713. [CrossRef] [PubMed]

7. Dave, P.N.; Pandey, N.; Thomas, H. Adsorption of Cr (VI) from aqueous solutions on tea waste and coconut husk. *Indian J. Chem. Technol.* 2012, 19, 111–117.

8. Aman, T.; Kazi, A.A.; Sabri, M.U.; Bano, Q. Potato peels as solid waste for the removal of heavy metal copper (II) from waste water/industrial effluent. *Colloids Surfaces B Biointerfaces* 2008, 63, 116–121. [CrossRef]

9. Elmolla, E.S.; Hamdy, W.; Kassem, A.; Abdel Hady, A. Comparison of different rice straw based adsorbents for chromium removal from aqueous solutions. *Desalin. Water Treat.* 2016, 57, 6991–6999. [CrossRef]

10. Chakraborty, R.; Asthana, A.; Singh, A.K.; Jain, B.; Susan, A.B.H. Adsorption of heavy metal ions by various low-cost adsorbents: A review. *Int. J. Environ. Anal. Chem.* 2020, 1–38. [CrossRef]

11. Afroz, S.; Sen, T.K. A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water Air Soil Pollut.* 2018, 229, 225. [CrossRef]

12. Shakoor, M.B.; Niazi, N.K.; Bibi, I.; Murtaza, G.; Kunhikrishnan, A.; Seshadri, B.; Shahid, M.; Ali, S.; Bolan, N.S.; Ok, Y.S.; et al. Remediation of arsenic-contaminated water using agricultural wastes as biosorbents. *Crit. Rev. Environ. Sci. Technol.* 2016, 46, 467–499. [CrossRef]

13. Ahmed, I.; Attar, S.J.; Parande, M.G. Removal of Hexavalent Chromium (Cr (VI)) from Industrial Wastewater by Using Biomass Adsorbent (Rice Husk Carbon). *Int. J. Adv. Eng. Stud.* 2012, 1, 92–94.

14. Park, D.; Yun, Y.S.; Ahn, C.K.; Park, J.M. Kinetics of the reduction of hexavalent chromium with the brown seaweed Ecklonia biomass. *Chemosphere* 2007, 66, 939–946. [CrossRef]

15. Bello, O.S.; Atiyebi, O.M.; Adegoke, K.A.; Fehintola, E.O.; Ojo, A.O. Removal of toxicant chromium (VI) from aqueous solution using different adsorbents. *J. Chem. Soc. Pak.* 2015, 37, 190.

16. Vempati, R.K.; Musthylala, S.C.; Mollah, M.Y.A.; Cocke, D.L. Surface analyses of pyrolysed rice husk using scanning force microscopy. *Fuel* 1995, 74, 1722–1725. [CrossRef]

17. Gao, W.; Li, H.; Karnowo; Song, B.; Zhang, S. Integrated Leaching and Thermochemical Technologies for Producing High-value Products from Rice Husk: Leaching of Rice Husk with the Aqueous Phases of Bioliquids. *Energies* 2020, 13, 6033. [CrossRef]

18. Basri, M.S.M.; Mustapha, F.; Mazlan, N.; Ishak, M.R. Optimization of Rice Husk Ash-Based Geopolymers Coating Composite for Enhancement in Flexural Properties and Microstructure Using Response Surface Methodology. *Coatings* 2020, 10, 165. [CrossRef]

19. Khalil, U.; Shakoor, M.B.; Ali, S.; Rizwan, M. Tea Waste as a Potential Biowaste for Removal of Hexavalent Chromium from Wastewater: Equilibrium and kinetic studies. *Arab. J. Geosci.* 2018, 11, 573. [CrossRef]

20. Shakoor, M.B.; Nawaz, R.; Hussain, F.; Raza, M.; Ali, S.; Rizwan, M.; Ahmad, S. Human health implications, risk assessment and remediation of As-contaminated water: A critical review. *Sci. Total Environ.* 2017, 601, 756–769. [CrossRef]

21. UCun, H.; Bayhan, Y.K.; Kaya, Y.; Cakici, A.; Algur, O.F. Biosorption of chromium (VI) from aqueous solution by cone biomass of *Pinus sylvestris*. *Bioreour. Technol.* 2002, 85, 155–158. [CrossRef]

22. ALOthman, Z.A.; Naushad, M.; Ali, R. Kinetic, equilibrium isotherm and thermodynamic studies of Cr (VI) adsorption onto low-cost adsorbent developed from peanut shell activated with phosphoric acid. *Environ. Sci. Pollut. Res.* 2013, 20, 3351–3365. [CrossRef] [PubMed]

23. Singaman, M. Removal of lead (II) and cadmium (II) ions from wastewater using activated biocarbon. *Sci. Asia* 2011, 37, 115–119. [CrossRef]

24. Sattar, M.S.; Shakoor, M.B.; Ali, S.; Rizwan, M.; Niazi, N.K.; Jilani, A. Comparative efficiency of peanut shell and peanut shell biochar for removal of arsenic from water. *Environ Sci Pollut Res.* 2019, 26, 18624–18635. [CrossRef] [PubMed]

25. Tajernia, H.; Ebadi, T.; Nasernegad, B.; Ghafori, M. Arsenic removal from water by sugarcane bagasse: An application of response surface methodology (RSM). *Water Air Soil Poll.* 2014, 225, 2028. [CrossRef]

26. Okafor, P.C.; Okon, P.U.; Daniel, E.F.; Ebenso, E.E. Adsorption capacity of coconut (*Cocos nucifera* L.) shell for lead, copper, cadmium and arsenic from aqueous solutions. *Int. Electrochem. Sci.* 2012, 7, 12354–12369.

27. Ali, I.H.; Al Mesfer, M.K.; Khan, M.I.; Danish, M.; Alghamdi, M.M. Exploring Adsorption Process of Lead (II) and Chromium (VI) Ions from Aqueous Solutions on Acid Activated Carbon Prepared from Juniperus procera Leaves. *Processes* 2019, 7, 217. [CrossRef]

28. Razmovski, R.; Šćiban, M. Biosorption of Cr (VI) and Cu (II) by waste tea fungal biomass. *Ecol. Eng.* 2008, 34, 179–186. [CrossRef]
29. Abid, M.; Niazi, N.K.; Bibi, I.; Farooqi, A.; Ok, Y.S.; Kunhikrishnan, A.; Ali, F.; Ali, S.; Igalavithana, A.D.; Arshad, M. Arsenic (V) biosorption by charred orange peel in aqueous environments. *Int. J. Phytoremediation* 2016, 18, 442–449. [CrossRef]

30. Sahmoune, M.N.; Louhab, K.; Boukhiar, A. Advanced biosorbents materials for removal of chromium from water and wastewaters. *Environ. Prog. Sustain. Energy* 2016, 18, 442–449. [CrossRef]

31. Pehliván, E.; Tran, H.T.; Ouedraogo, W.K.I.; Schmidt, C.; Zachmann, D.; Bahadir, M. Sugarcane bagasse treated with hydrous ferric oxide as a potential adsorbent for the removal of As(V) from aqueous solutions. *Food Chem.* 2013, 138, 133–138. [CrossRef]

32. Ahmad, M.; Lee, S.S.; Rajapaksha, A.U.; Vithanage, M.; Zhang, M.; Cho, J.S.; Lee, S.E.; Ok, Y.S. Trichloroethylene adsorption by pine needle biochars produced at various pyrolysis temperatures. *Bioresour. Technol.* 2013, 143, 615–622. [CrossRef] [PubMed]

33. Nadeem, R.; Manzoor, Q.; Iqbal, M.; Niraj, J. Biosorption of Pb (II) onto immobilized and native Mangifera indica waste biomass. *J. Ind. Eng. Chem.* 2015, 35, 185–195. [CrossRef]

34. Nadeem, R.; Manzoor, Q.; Iqbal, M.; Nisar, J. Biosorption of Pb (II) onto immobilized and native Mangifera indica waste biomass. *J. Ind. Eng. Chem.* 2015, 35, 185–195. [CrossRef] [PubMed]

35. Ali, S.; Rizwan, M.; Shakoor, M.B.; Jilani, A.; Anjum, R. High sorption efficiency for As (III) and As (V) from aqueous solutions using novel almond shell biochar. *Chemosphere* 2020, 243, 125330. [CrossRef] [PubMed]

36. Owalude, S.O.; Tella, A.C. Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. *Beni-Suef Univ. J. Basic Appl. Sci.* 2016, 5, 377–388. [CrossRef]

37. Vinodhini, V.; Das, N. Mechanism of Cr (VI) biosorption by neem sawdust. *Am.-Eurasian J. Sci. Res.* 2009, 4, 324–329.

38. Khazaeei, I.; Aliabadi, M.; Hamed, M.H. Use of agricultural waste for removal of Cr(VI) from aqueous solution. *Iran. J. Chem. Eng.* 2011, 8, 11–23.

39. Singha, B.; Naiya, T.K.; Kumar, B.A.; Das, S.K. Cr (VI) ions removal from aqueous solutions using natural adsorbents–FTIR studies. *J. Environ. Prot.* 2011, 2, 729. [CrossRef]

40. Yi, Y.; Lv, J.; Liu, Y.; Wu, G. Synthesis and application of modified Litchi peel for removal of hexavalent chromium from aqueous solutions. *J. Mol. Liquids* 2017, 225, 28–33. [CrossRef]

41. Peng, S.H.; Wang, R.; Yang, L.Z.; He, L.; He, X.; Liu, X. Biosorption of copper, zinc, cadmium and chromium ions from aqueous solution by natural foxtail millet shell. *Ecotoxicol. Environ. Saf.* 2018, 165, 61–69. [CrossRef] [PubMed]

42. Rosales, E.; Mejide, J.; Tavares, T.; Pazos, M.; Sanromán, M.A. Grapefruit peelings as a promising biosorbent for hexavalent chromium removal. *Proc. Saf. Environ. Prot.* 2016, 101, 61–71. [CrossRef]

43. Vu, X.H.; Nguyen, L.H.; Van, H.T.; Nguyen, D.V.; Nguyen, T.H.; Nguyen, Q.T.; Ha, L.T. Adsorption of Chromium (VI) onto Freshwater snail shell-derived biosorbent from aqueous solutions: Equilibrium, kinetics, and thermodynamics. *J. Chem.* 2019. [CrossRef]

44. Ghaneian, M.T.; Bhatnagar, A.; Ehrampoush, M.H.; Amrollahi, M.; Jamshidi, B.; Dehvari, M.; Taghavi, M. Biosorption of hexavalent chromium from aqueous solution onto pomegranate seeds: Kinetic modeling studies. *Int. J. Environ. Sci. Technol.* 2017, 14, 331–340. [CrossRef]

45. Hu, H.; Gao, Y.; Wang, T.; Sun, L.; Zhang, Y.F.; Li, H. Removal of hexavalent chromium, an analogue of pertechnetate, from aqueous solution using bamboo (*Acidosasa edulis*) shoot shell. *J. Radioanal. Nucl. Chem.* 2019, 321, 427–437. [CrossRef]

46. Aman, A.; Ahmed, D.; Asad, N.; Masih, R.; Abd ur Rahman, H.M. Rose biomass as a potential biosorbent to remove chromium, mercury and zinc from contaminated waters. *Int. J. Environ. Stud.* 2018, 75, 774–787. [CrossRef]

47. Xie, Y.; Li, H.; Wang, X.; Ng, I.S.; Lu, Y.; Jing, K. Kinetic simulating of Cr (VI) removal by the waste Chlorella vulgaris biomass. *J. Taiwan Inst. Chem. Eng.* 2014, 45, 1773–1782. [CrossRef]