# pH Dependent Hexavalent Chromium Adsorption Experiments by Biochar Derived by Rice Husk

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https://doi.org/10.5109/7323408

出版情報：Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES). 10, pp.1192-1197, 2024-10-17. International Exchange and Innovation Conference on Engineering & Sciences
バージョン：

# pH Dependent Hexavalent Chromium Adsorption Experiments by Biochar Derived by Rice Husk

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**Abstract:** *Rice husks (RHs) is a low-cost biowaste that has been widely studied for a few decades. In environmental remediation field, rice husks can be used to removal heavy metals as an adsorbent. And plenty of modification have been implemented on rice husks. In this study, the adsorption capacity of RHs and modified RHs was investigated by conducting Chromium (VI) adsorption experiments at different pH conditions. The results show that the carbonization of RHs helps little with the adsorption capacity to Chromium (VI). However, the chemical modification by sodium hydroxide plays a significant role in the heavy metal removal tests, which increase the removal rate from 30% to 84% at pH 3, comparing to raw RHs. Also, lower pH was confirmed as the most appropriate condition for Chromium(VI) removal.*

**Keywords:** Rice husks; Hexavalent chromium; Chemical modification; Adsorption; Biochar

## 1. INTRODUCTION

The earth is confronting numerous challenges regarding resources, energy, and pollution. As far as contamination in water is concerned, there are various categories of pollutants, for example, inorganic contaminants including phosphorus[1-4], nitrogen[4], chromium[5, 6], arsenic[7], and so on, existing in different water bodies.

Novel technologies (e.g. membrane technology, nanotechnology, and so on) have been developed to recover the edible part of water and achieve the standard of drinking water by treating wastewater or contaminated water through sustainable development methods. Also, the modeling of solute transport[8,9] was also been studied in the environmental geology field.

Environmental nanotechnology is a cutting-edge technique that plays a significant role in the remediation of water and soil systems due to its unique properties of microstructures. Nano zero-valent iron (nZVI) is a popular topic so that many research has been done on it, including coating with other materials (e.g., magnesium hydroxide[5,10], graphene[11], and zeolite[12]) to form composites or chemically deposing on other nanomaterial, nanowires[13]. Amen[14] also studied the effect of nZVI on methane production microorganisms and Khalil[15] focused on the regeneration of nZVI spent in water remediation. It also significantly contributes to the success of adsorption technology development.

Adsorption technology has been studied for a long time period since the 20th century and applied to thousands of raw materials(e.g., Chlorella vulgaris[7]).Activated carbon has now been well explored and commercially utilized due to its high surface area and relatively low cost of production. More carbon-based adsorbents have been developed among plants, fruits, and other biomaterials.

Rice husks are usually produced by rice processing factories as a wasted biomaterial and a huge amount of research has been done on not only the application of rice husks but also the modifications of rice husks as adsorbents. As for modifications, plenty of methods are investigated including combining with nanocomposites and treating with acidic or alkaline solutions after carbonization. Noticeable facts were highlighted by Ahma [16] saying that different types of biochar have distinct adsorption capacities to specific heavy metals. Even as for the same raw material, for instincts, rice husks and the rice straws are unlikely each other.

In this paper, rice husks are further studied by alkaline modification after carbonization to remediate water from heavy metal contamination hexavalent chromium Cr(VI).

## 2. MATERIAL AND METHODS

### 2.1 Reagents

All reagents utilized in this experiment were of analytical grade. All water was deionized and purified by (Machine name) and the pH is around 5.5. Sodium hydroxide (NaOH, 97%) was purchased from Junsei Chemical Co., Ltd, Japan. Hydrochloric acid(HCI, 35-37%,) was purchased from Wako, Japan. Potassium dichromate (≥ 99.5%) was purchased from Sigma-Aldrich, Japan.

Rice husks(RHs) were collected from local factories in Fukuoka, Japan.

### 2.2 Preparation of powdered rice husks

Rice husks were washed with deionized water to remove the dust and impurities three times and then placed into a dryer at 60°C until the weight was no longer changed. These raw materials without further milling were labeled as RHs. The dried RHs were then transferred into a wonder crusher(WC-3L) to shred rice husks into powder and the obtained powders were sieved with a #50 mesh to constrain the diameters of the powders to less than 300 um. The ultimately obtained material was stored and labeled as pRH(<300μm) and the materials retained on the sieve were stored and labeled as pRH(>300μm). pRH(<300μm) was simplified as pRH.

### 2.3 Preparation of carbonized rice husk

RHs and pRHs were transferred into a tube furnace (TF1 11/32/150, Carbolite GERO Ltd.,) and glass wool was placed at two ends of the material in order to gather the material at the center of the quartz tube. The tube furnace was heated at a ramping rate of 5°C/min from room temperature to 400°C and the high temperature was

dwelled for an hour under a nitrogen environment.


Fig. 1. Image of tube furnace (TF1 11/32/150, Carbolite GERO Ltd.,)

Finally, the material was normally cooled to room temperature. The nitrogen flow rate was consistent and maintained until the material was cooled to room temperature inside the tube furnace. And the obtained materials were labeled as RHC400 and pRHC400, respectively.

### 2.4 Preparation of modified rice husk


Fig. 2. Images of (a) RHs, (b) pRH(>300μm), (c) pRH, (d) pRHC400, (e) RHC400, and (f) pRHC400N700

As for the chemical activation, all pre-carbonized RHs were immersed in 5 wt % of sodium hydroxide solution for 24 hours with the magnetic bar stirring. A 0.45-micrometer membrane was used to filter the sodium hydroxide out from the biochar through a vacuum pump. Then the alkaline modified pRHs were directly placed in the tube furnace in a 10ml-quartz boat, and the furnace was heated up to 400°C with the ramping rate of 5°C/min and dwelled for 30 mins and then kept heating up to 700°C and dwelled for 1 hour. Next, the activated pRHs were cooled to room temperature and washed with 1M HCl solution. Once no bubbles were purged, the biochar was washed with DI water until the pH of the wasted water was around 5.5. An oven was finally used to dry the biochar at 105°C to remove all the water content. The obtained material was labeled as pRHC400N700.
All the materials produced in this study were stored in sealed polyethylene bags before use.

Table 1. Summary of RHs, pRHs and pRH(>300μm)

| Label | Material | Modification |
|---|---|---|
| RH | Raw Rice Husk | No |
| pRH(>300μm) | Powdered Rice Husk | Machine crushing, not passed the #50 sieve |
| pRH | Powdered Rice Husk | Machine crushing, passed the #50 sieve |
| RHC400 | RH | Carbonized at 400°C |
| pRHC400 | pRH | Carbonized at 400°C |
| pRHC400N700 | pRHC400 | Activated by NaOH and treated at 700°C |

### 2.5 Preparation of chromium(VI) stock solution

1g/L of Cr(VI) stock solution was prepared by adding 2.8287 grams of K2Cr2O7 into 1L of deionized water.

### 2.6 Batch experiment

The dosage of the adsorbent was determined to be 1g/L. The batch experiments were conducted in 200 ml solution, prepared by adding 10 ml of stock solution and 190 ml of deionized water into each flask where the Cr(VI) concentration was diluted to 50mg/L. Those flasks were placed on a magnetic base that guaranteed the experiments were performed at 1000 rpm stirring rate and 25°C.
1ml of the sample was extracted from each flask at specific time and then filtered with 0.45μm membrane diluted to test the Cr(VI) concentration using the HACH DR 3900 VIS Spectrometer.
All the samples were stored in the refrigerator in case there is further need.

### 2.7 X-ray Diffraction Analysis

The x-ray diffraction(XRD) analysis was conducted to determine the elements contribution and the crystallinity of the rice-husk derived biochar.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Production rate

The production rate of the carbonization process that transformed raw material into biochar is calculated to be around 50%, which is shown in Table 1 based on the equation below.

$$Production\ Rate = \frac{Initial\ weight - Final\ weight}{Initial\ weight}\ x\ 100\% \quad (1)$$

Table 2. Production rates of RH and pRH

| Material | Initial Weight(g) | Final Weight(g) | Production Rate (%) |
|---|---|---|---|
| *RHC400* | 10.3521 | 4.3112 | 41.6 |
| *pRHC400* | 21.278 | 11.136 | 52.3 |

### 3.2 Preliminary experiments

The initial pH and final pH of the solution were measured as 5.0 ± 0.1 and 5.6 ± 0.2, respectively.
And due to the pH effect from the DIW, the initial concentration of Cr(VI) is shifted from 50mg/L, the expected value, to around 43mg/L. The corresponding

effects are discussed later.
According to Figure 3, pRH(>300μm) and pRH showed similar adsorption capacity for hexavalent chromium removal based on the 2 and 24-hour results.

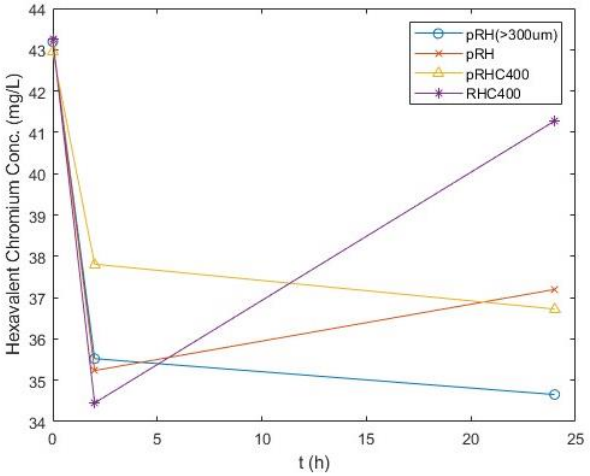


Fig. 3. Hexavalent chromium concentrations after adsorption by pRH(>300μm), pRH, pRHC400, and RHC400 within 24hrs under normal pH and room temperature

The pRH(>300μm) and pRH particles are all produced by the wonder crusher at once so the properties are consistent except the size. And the size difference between the two materials is not very significant. The results demonstrate that the non-noticeable size difference would not have a huge effect on the adsorption capacities under this specific experimental condition.
Surprisingly, the carbonized rice husk shows a slightly lower adsorption capacity than those two raw materials. It may be caused by the holes synthesized during carbonization that had not been activated yet. Nguyen et al.[17] found that the unactivated biochar usually has a weakness of poor surface chemistry and small surface area, which means that the carbonization even destroys the binding sites for hexavalent chromium removal. Zhang et al. proposed that Cr(VI) could be reduced by the alkenes functional group on the surface of the biochar. FTIR spectroscopy is the most recommended and suitable methodology to prove the mechanism further.
Sumashi et al.[18] found the same results that natural rice husk has 30 percent removal rate to Cr(VI).
In general, the four types of materials showed relatively similar capacities for Cr(VI) removal, which is 7 ± 1.7 mg/L and shown in Figure 4. The values of adsorption capacities of pRH(>300μm), pRH, RHC400 and pRHC400 are 8.346, 7.765, 6.277, and 8.550 mg/g, respectively.

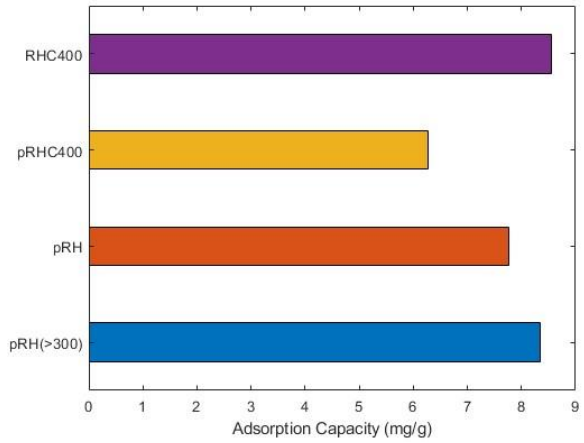


Fig. 4. Adsorption capacities of pRH(>300μm), pRH, RHC400 and pRHC400 at normal pH for Cr(VI) Removal
A control group was performed without any variables under the same experimental circumstances as the other batch tests.

### 3.3 pH-dependent adsorption experiments

Sodium hydroxide and hydrochloric acid were used to adjust the pH of the solution.

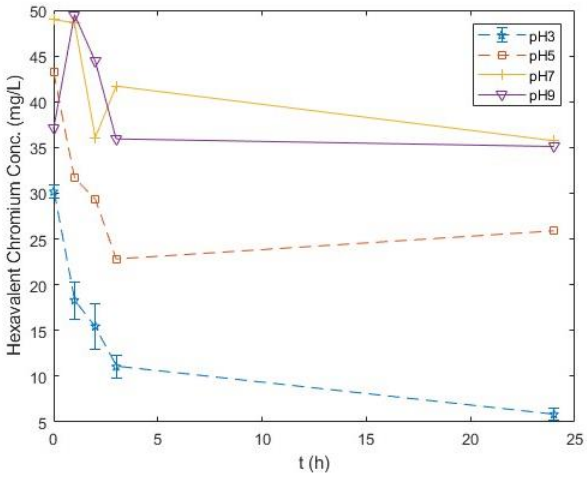


Fig. 5. Initial and final hexavalent chromium concentrations at pH 3, pH 5, pH 7, and pH 9 from 0 to 24hrs with dosage of 1g/L pRHC400N700 and 50mg/L initial under room temperature

When pH drops to 3, the initial concentration of Cr(VI) dramatically decreases compared to those at higher pH, which is about 29mg/L. Due to the huge distinction between this group and the others, the adsorption test at pH 3 was performed twice to ensure the reliability of the results. The batch experiment conducted at pH 3 by 1 g/L pRHC400N700 with 50mg/L initial concentration was repeated one more time. The final Cr(VI) concentration was determined as the average value of both the original and new data, which were shown as error bar in the Fig. 5.
The results confirm that the observation is reasonable and the adsorption capacity at lower pH is undoubtedly great. Compared to the atomic size of Cr(VI), that of Cr(III) is smaller and it is more easily absorbed by the micropores of biomass under acidic conditions[19]. The great removal capacity could also be caused by the different initial concentrations of Cr(VI), 29mg/L, which is much less than that from the other experimental groups.

Boshnoi et al[20] found that the rick husk activated at 300°C for 30 mins has the best Cr(VI) removal rate when pH is 2. The results show a slight difference with this study, which discovered that 3 is the best pH for Cr (VI) removal. However, we have to mention that the methodologies between the two papers are different. In the former paper, 10ppm Cr(VI) solution and 10g/L dosage of biochar were utilized to perform the experiments, which is distinct from that of this study, which is 50mg/L of Cr(VI) and 1g/L of biochar, respectively. The lowest pH studied in this paper was 3 and the value in Boshnoi et. al's paper was 2. Zhang et al.[19] also reported that the removal efficiency of Cr(VI) by modified rice husk has the best performance at the lowest pH, and the predominant mechanism is the reduction reaction that reduces the Cr(VI) to Cr(III). Based on this trend, we can conclude that the lowest pH in acidic conditions would have the best Cr(VI) removal rate according to the mechanism(Eq.(2) and Eq.(3)), the hexavalent chromium was reduced to trivalent chromium at low pH, which was proposed by Sharma and Forster.

$$7H^+ + HCrO_4^- + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad (2)$$

$$8H^+ + CrO_4^{2-} + 3e^- \rightarrow Cr^{3+} + 4H_2O \quad (3)$$

When the concentration of protons increases, the reversible reaction moves forward and more Cr(VI) is reduced to Cr(III). And Stern et. al[21] reported the electric potential of Cr(VI) at acidic conditions is strong(e.g., $E^0(HCrO_4^-/Cr^{3+}) = 1.35V_{NHE}$ ).

Regarding the reduction reaction occurring at low pH, measuring the total chromium concentration could be a straightforward approach to explain the phenomenon.

Comparing the results of the control group and experimental group at pH 3, due to the influx of pRHC400N700, the concentrations of the experimental group decreased by 10 mg/L. The potential mechanism could be attributed to the fact that the final washing process of biochar was conducted by DIW which is slightly acidic and the surface charge of the biochar thus was positive so that the pH at this time fell. Thus, the Cr(VI) was further transferred to Cr(III) so that the concentrations drops down. Another potential mechanism could be the reduction reaction carried out by the alkenes on the surface of the biochar.

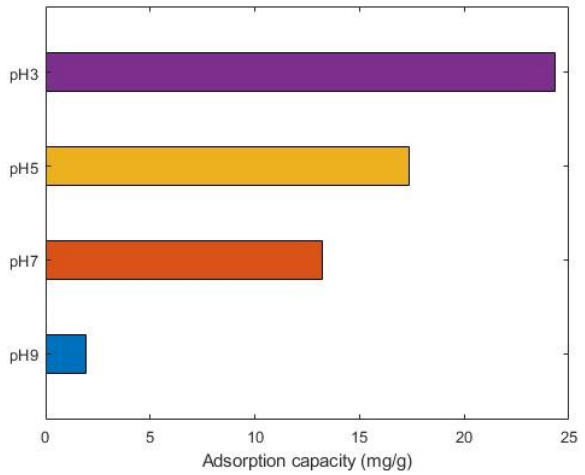


Fig. 6. Adsorption capacities of pRHC400N700 at pH 3, pH 5, pH 7 and pH 9 with dosage of 1g/L and initial Cr(VI) concentration of 50mg/L under room temperature

The adsorption capacities of pRHC400N700 at pH 3, pH 5, pH 7 and pH 9 were calculated as 24.336, 17.339, 13.226, and 1.954 mg/g, respectively, and shown in Figure 6. When pH rises to the neutral condition, the initial concentrations reach the highest level, around 49mg/L, which is close to the expected initial value, 50 mg/L.

Table 3. Initial and final pH of each experimental groups, at pH 3, pH 5, pH 7 and pH 9 from 0 to 24hrs

| Experimental Group | Initial pH | Final pH |
|---|---|---|
| pH3 | 3 | 3.41 |
| PH5 | 5 | 6.34 |
| pH7 | 7 | 7.47 |
| pH9 | 9 | 7.79 |

Based on all the results in this paper, almost all of the values of final pH rise compared to that of the initial ones because the protons in the solution were consumed by Cr(VI) except in alkaline conditions. The exception may be caused by the precipitation of $Cr(OH)_3$, where the Cr(III) ions was produced due to the reactions on the surface of the biochar at alkaline conditions. This phenomenon needs further experiments to prove.

Also, an observation was found that the concentrations of Cr(VI) after 24 hours of experiments would elevate slightly. The potential mechanism may be attributed to the desorption process occurring after long time magnetic stirring. However, Sumathi et al.[18] reported that the adsorption process continued from 0 to 48hrs without losing the adsorption capability. The possible reason caused this phenomenon was that the dosage used in Sumathi's paper was much more than that of this paper, which means that there were more binding sites or free space on the surface of the biochar and had not been achieving the maximum adsorption. Moreover, most of the papers that used small dosage often lacked the data about the concentrations at 24hrs and the reason may be those abnormal data influenced by the desorption process.

### 3.4 XRD Results

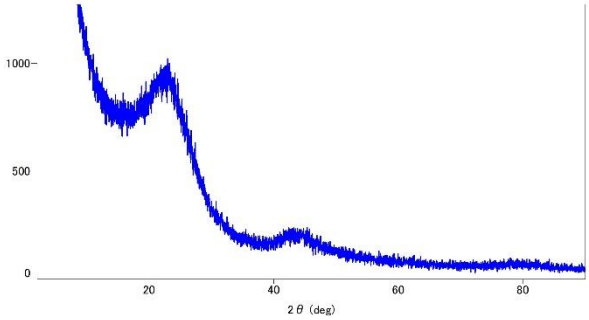


Fig. 7. XRD result of pRHC400N700

Based on Fig. 7, the XRD result shows that there are two obvious peaks, whose 2Θ = 22.96° and 45.4°, respectively. The first peak could be attributed to the carbon element which is the middle state of amorphous carbon, around 20°, and graphitic carbon, around 26°[22]. And the peak at 45.4° may reflected that the sodium chloride crystallinity was left onto the biochar when the pRHC400N700 was washed with 1M HCl solution after modifying by NaOH solution and precipitated out when the pRHC400N700 was dried at 105°C.

## 4. CONCLUSIONS

The Cr(VI) removal capacities of RHs and modified RHs are pH-dependent based on the results in this paper. The physical modification, shredding into finer particle sizes, does not affect the adsorption capacity to Cr(VI) much. Even the performance of the rice husk carbonized at 400°C, pRHC400, is not greater than those undergo physical modifications, pRH(>300μm) and pRH. At lower pH, the pRHC400N700, which was modified by sodium hydroxide, carbonized at 400°C, and activated at 700°C, has the greater adsorption capacity to Cr(VI) comparing to neutral and alkaline conditions. The ultimate concentration of Cr(VI) at neutral and alkaline conditions is related highly to the final pH of the solution and the adsorption capacity of biochar. The best pH for removal of Cr(VI) was determined as the lowest pH value, which is 3 in this study.

## 5. FURTHER STUDIES

In this paper, the adsorption mechanism remains unclear and the adsorption categories, chemical or physical adsorption, are also unexplored. The desorption test is a good way to distinguish the exact types of adsorptions. Also, the effect of various initial concentrations, dosages, ionic strengths, and temperatures, on the adsorption process was significant to investigate the adsorption mechanism in depth.

Further studies could be performed fol1owing the instructions mentioned above.

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