Adsorption of Hg(II) in an Aqueous Solution by Activated Carbon Prepared from Rice Husk Using KOH Activation

Zhiyuan Liu, Yong Sun, Xinrui Xu, Jingbo Qu, and Bin Qu

ABSTRACT: With the development of industry, the discharge of wastewater containing mercury ions posed a serious threat to human health. Using biomass waste as an adsorbent to treat wastewater containing mercury ions was a better way due to its positive impacts on the environment and resource saving. In this research, activated carbon (AC) was prepared from rice husk (RH) by the KOH chemical activation method. The characterization results of scanning electron microscopy (SEM), Brunauer−Emmett−Teller (BET), Fourier transform infrared (FTIR), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) showed that rice husk-activated carbon (RHAC) had good pore structure and oxygen-containing functional groups. The influences of contact time, initial concentration of Hg(II), adsorbent dosage, pH, and ionic strength on mercury ion removal were investigated. The Langmuir model was most suitable for the adsorption isotherm of RHAC, and its maximum adsorption capacity for Hg(II) was 55.87 mg/g. RHAC still had a high removal capacity for Hg(II) after five regeneration cycles. RHAC had excellent removal efficiency for mercury ion wastewater. At the same time, RH could be used as a nonpolluting and outstanding characteristic adsorbent material.

1. INTRODUCTION

The problem of heavy-metal pollution in water bodies was becoming increasingly prominent.1–3 The most urgent task of improving the water environment was to reduce heavy-metal pollution. The discharge of industrial wastewater led to the heavy-metal content exceeding the standard for many waters, which was the leading cause of heavy-metal pollution.4 In addition, metals in the soil entered the water surface through rainfall and other means, polluting the groundwater and severely affecting drinking water sources.4 Excessive levels of heavy metals could affect embryonic development and human nervous tissue and cause severe diseases such as cancer and cardiovascular disease.4–9 Mercury was the most harmful heavy metal among water pollutants, known as the first kind of pollutants.9 The discharge of industrial wastewater, such as chlor-alkalization, amalgam, and switch equipment, was the main cause of mercury pollution.10 Once this kind of wastewater is transmitted to the human body through the food chain, it can pose significant health risks.11,12

The methods of removing heavy-metal pollution in water generally included chemical precipitation, membrane separation, ion exchange, electrodialysis, and adsorption.13 The adsorption method was characterized by convenient operation, low operation cost, and no secondary pollution.14–16 AC adsorption has its own physical and chemical characteristics, which could provide adsorption sites.17–19 The adsorption−desorption method could simultaneously treat water heavy-metal pollution and regenerate the adsorbent. To further improve the ability to remove heavy-metal ions, the activation method was usually adopted to increase its oxygen-containing functional groups.20 The commonly used chemical activators included H2SO4, H3PO4, ZnCl2, NaOH, and KOH.21–25 KOH

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could adjust the pore structure of AC, promoting the generation of micropores and the formation of $-\text{OH}$; the specific surface area will be significantly increased and further improve the adsorption capacity.\textsuperscript{26,27}

In recent years, the preparation of AC using agricultural waste has been in full swing in all kinds of research.\textsuperscript{28} Coconut shells, apricot shells, walnut shells, and green vegetable waste have been used as raw materials to remove metal ions.\textsuperscript{29–33}

Figure 1. (a, b) SEM graphs, (c) nitrogen adsorption–desorption isotherm, (d) pore size distribution, (e) Raman spectra, and (f) FTIR spectra of rice husk-activated carbon (RHAC).
The reason is that these raw materials are low in cost and have a certain ability to adsorb metal ions. Research on materials for removing mercury ions is also in progress. The maximum amount of mercury ions adsorbed by the researchers under static and dynamic conditions was 28.00 mg/g using Spanish broom as the raw material. Other researchers had prepared three-dimensional graphene oxide by combining several functional groups, and its adsorption capacity was 35.00 mg/g. The above-mentioned research had low efficiency in removing mercury ions. In addition, glycicyl methacrylate was prepared in several steps. Although it had considerable adsorption capacity, its preparation method was complex.

Since the current preparation method of activated carbon had drawbacks such as a complicated process and high energy consumption, in this study, rice husk (RH) with wider sources, lower price, and easier collection was used to prepare economical and effective biochar adsorbent by an uncomplicated process. An adsorbent with both adsorption capacity and recyclability was developed, which provided a worthy method for mercury ion adsorption. China is the largest rice producer in the world. The rice production was about 210 million tons in 2019, and RH accounted for about one-fifth of the quality of rice. In grain processing enterprises, the treatment and effective utilization of RH had become an urgent problem. The mass fraction of carbon in rice husk had gone over 50%, indicating that it is a good material for biochar and it could potentially be used to prepare high-quality activated carbon. RH could be carbonized to form a pore structure, which is conducive to the adsorption of metal ions. At the same time, the amount of oxygen-containing functional groups on the surface of biochar increased after the carbonized biochar was mixed with an activator and heated, which further enhanced the adsorption capacity.

The AC used in this work was prepared from RH by potassium hydroxide activation. The effects of contact time, pH, initial concentration of Hg(II), adsorbent dosage, and ionic strength were studied by adsorption experiments. The surface morphology, porous structure, graphitization, surface functional groups, and chemical composition of AC were characterized by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), Raman spectroscopy, Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS). The equilibrium and kinetic data were discussed. The adsorption mechanism was also analyzed.

2. RESULTS AND DISCUSSION

2.1. Characterization of Activated Carbon. The microstructure of modified AC was characterized by SEM. As can be seen in Figure 1a,b, the surface of AC was rough and it presented irregular circular pore structures. Abundant pores could improve its adsorption performance for metal ions.

Pore size distribution was the critical factor to characterize porous carbon. The porous carbon structure was determined by N2 adsorption/desorption isotherms. It can be seen from Figure 1c that the N2 adsorption/desorption isotherms were type I and IV hybrids, indicating that there were many micropores in the adsorbent. The rapid rise of adsorption–desorption isotherms in the low-pressure region also indicated that there were microporous or small mesoporous structures. It showed that microporous and small mesoporous structures played an important role in the adsorption of pollutants. In Table 1, the surface area and pore volume data are presented. The specific surface area of RHAC was 887.32 m2/g, which was higher than that of other studies. As shown in Figure 1d and Table 1, micropore (<2 nm) and mesopore (2–50 nm) structures existed in RHAC, and the micropore volume accounted for 72.92% of the total pore volume. The porous carbon with smaller pore sizes ensured higher diffusion and adsorption rates.

Raman spectroscopy is a vital method to analyze the internal chemical structure of AC. The D-band and G-band emerged at around 1339 and 1590 cm−1, respectively, as shown in Figure 1e. The D-band was considered to be a disordered vibration peak of carbon materials. The G-band was used to characterize the integrity of the sp2 hybrid bond structure in the graphite structure. The graphitization degree or defects of carbon material were calculated by the intensity ratio of the D-band and the G-band (I\textsubscript{D}/I\textsubscript{G}). The I\textsubscript{D}/I\textsubscript{G} value was 0.96, indicating that RHAC had a reasonable degree of graphitization.

The chemical groups of the samples were studied by FTIR spectra, and the results are shown in Figure 1f. The peak at around 1100 cm−1 represented the C–O band found in ester and phenol. The band of 1490 cm−1 was the skeleton vibration of C=C on the aromatic ring. The band at 2930 cm−1 was due to asymmetric and symmetrical extension of CH2 groups in lignin, cellulose, and hemicellulose. A broad band of the −OH stretching vibration near 3440 cm−1 in the presence of alcohol, phenol, or carboxylic acid was observed. The presence of carbonyl groups, lactones, aldehydes, and carboxyl groups of AC was explained by these bands. The abundance of acidic functional groups could make available adsorption sites for AC, which led to an increase in adsorption capacity.

XPS is a widely applied surface chemical analysis technology that is used to obtain specific element information in materials. The detailed XPS measurements of the C 1s, O 1s, and Hg 4f regions of RHAC are shown in Figure 2a. It could be seen that the main elements in RHAC were C 1s (284.0 eV) and O 1s (531.0 eV). For the C 1s (Figure 2b), there was a strong peak at 284.0 eV, which was attributed to C=C. The other peaks of C 1s were at 285.2 and 288.3 eV with C–O and C=O, respectively. The 1s peak of carbon materials was centered on the binding energy of 284.2, 285.6, and 288.6 eV, respectively, in Figure 2d. Moreover, the O 1s spectrum of RHAC after adsorption (Figure 2e) was also composed of three fitting peaks of C=O, C=O, and C–O.
H−O, and C−O at 530.2, 531.9, and 533.3 eV, respectively. It could be found that C and O had a certain chemical shift after the adsorption of mercury ions, indicating that they were all involved in the adsorption process. Two peaks at 100.8 and 104.8 eV are shown in Figure 2f, which may be attributed to the presence of Hg 4f$_{7/2}$ and 4f$_{5/2}$.

Figure 2. XPS spectra of (a) survey, (b) C 1s, (c) O 1s, (d) C 1s after adsorption, (e) O 1s after adsorption, and (f) Hg 4f after adsorption of RHAC.
mercury was adsorbed in an oxidized state, indicating that the main adsorption mechanism of mercury ions was oxidative chemisorption. It further illustrated the important role of oxygen-containing functional groups in the adsorption of mercury ions.

2.2. Method Optimization. 2.2.1. Effect of Contact Time. Tests were carried out at different contact times (15, 30, 60, 90, and 120 min). The Hg(II) initial concentration was 8.0 mg/L, at a pH of 5.0 and 25 °C. The dose of the adsorbent was 0.02 g. The results are shown in Figure 3a. Both the adsorbents had a faster adsorption speed in the first 15 min; the $q_e$ was 19.20 and 2.96 mg/g, respectively. The surface of the adsorbents had a high concentration of free active sites, so the adsorption speed was very fast at the beginning. Most of the active sites of the adsorbent surface were occupied, and the Hg(II) concentration decreased, causing a slower adsorption rate after 15 min. It could be seen that equilibrium was basically achieved at 60 min. The adsorption capacity of RHAC on Hg(II) was 34.80 mg/g, which was significantly higher than
that of RHC (5.88 mg/g). Based on the adsorption results and the above analysis, 60 min was regarded as the most suitable time for the experiment. RHAC not only had a higher adsorption capacity than previous studies but also had a faster adsorption speed for mercury ions.54

2.2.2. Effect of pH. pH had a very significant effect on adsorption. The pH value range was 2.0−6.0; other parameters: the initial concentration of Hg(II) was 8.0 mg/L, and RHAC and RHC were 0.02 g.

When the pH was low, the adsorption capacity of both adsorbents was deficient. Because of competitive adsorption between H+ and Hg(II), most of the adsorption sites were occupied by H+ under strongly acidic conditions. However, as the pH value increased, the concentration of H+ decreased, and the binding ability of Hg(II) to the adsorbent surface was enhanced. According to Figure 3b, when the pH value was increased from 2.0 to 5.0, the adsorption capacities of RHAC and RHC increased from 9.64 and 4.96 to 34.80 and 5.88 mg/g, respectively. When pH was higher than 5.0, the adsorption capacity of Hg(II) decreased significantly, which might be due to the formation of hydroxides of mercury. By detecting the pHpzc of the adsorbent, the optimal pH value for adsorption could be roughly determined. When the solution pH < pHpzc, the surface of the adsorbent was positively charged, which caused electrostatic repulsion with metal cations in the solution and inhibited the adsorption. When the solution pH > pHpzc, the surface of the adsorbent was deprotonated and the adsorption capacity for mercury ions was enhanced. According to Table 1, the pHpzc value of RHAC was 3.23. It can be seen that the adsorption efficiency of RHAC for mercury ions increased significantly when pH was greater than 3.0. As shown in Table 4, the optimum pH value of adsorption varies with the materials and modification methods of different adsorbents.

2.2.3. Effect of Adsorbent Dosage. The AC dosage was 0.2−1.0 g/L; other parameters: 25 °C, pH of 5.0, initial concentration of Hg(II) was 8.0 mg/L.

From Figure 3c, it can be seen that when RHAC was added at 0.2 g/L, the adsorption capacity was the largest. The increase of the adsorption capacity was owing to the large surface area and adsorption sites of AC. However, RHC provided fewer adsorption sites, resulting in an adsorption capacity of only 1/6 of RHAC. After a 0.2 g/L adsorbent dose was added, the adsorption capacity of Hg(II) decreased, which was mainly due to the excess of active centers provided by AC; it reduced the adsorption capacity per unit mass. Moreover, excessive dosage of AC will reduce the mixing efficiency and interfere with the mass-transfer process, thereby affecting the adsorption process.55 Considering the ecological environment, lower dosages of adsorbents could reduce the negative impacts on the environment. Compared with the several adsorbents listed in Table 4, RHAC was a better choice for treating mercury ions in wastewater.

2.2.4. Effect of the Initial Hg(II) Concentration. The influence of the initial concentration of Hg(II) was studied. The conditions were as follows: 0.02 g of adsorbent was added and pH was 5.0. Figure 3d shows the changes in the adsorption capacity when the initial concentrations of Hg(II) were in the range 4.0−20.0 mg/L.

The adsorption capacity of an adsorbent can be seen more directly by the concentration of adsorbate. Researchers selected different concentrations of adsorbates to explore their effects on mercury adsorption.56 The qe of the two adsorbents increased with the increase of the initial concentration of Hg(II). Since the solute concentration was low at the beginning, the ratio of the solute concentration to the surface area of the adsorbable solute was low. With the increase of solution concentration, the binding sites were more fully utilized by the adsorbate, which increased the adsorption capacity. Since the adsorption sites on RHC were limited, the adsorption capacity was only 7.40 mg/g when the concentration was 20.0 mg/L. When the concentration of mercury ions exceeded 12.0 mg/L, the upward trend of adsorption capacity was slow. As the number of active groups on RHAC and RHC was limited, the adsorbent will not continue to adsorb at this concentration or higher.

2.2.5. Effect of Ionic Strength. It is known that industrial wastewater contains a large amount of salt. In this study, different concentrations of potassium chloride were used to explore the effects of ionic strength. RHAC was put into 100 mL of an aqueous solution containing Hg(II) (8.0 mg/L) and stirred (150 rpm); pH was 5.0 and the contact time was 60 min.

As shown in Figure 3e, there was almost no effect on the mercury ions in the adsorption solution when the concentration of potassium chloride or sodium chloride was low. However, when the concentration was higher than 0.05 mol/L, it had an inhibitory effect on the experiment. This was because K+ and Na+ occupied the adsorption sites or Cl− complexed with Hg(II), which interfered with the removal of Hg(II). Besides, K+ had a greater influence on the adsorption of mercury ions than Na+. This is because in an aqueous solution, the smaller the radius of the hydrated ion, the higher the charge and the greater the affinity. Therefore, K+ had a stronger ability to compete for adsorption sites than Na+.

2.3. Kinetic Studies. To further explore the mechanism of mercury ions in RHAC, the following models were included: pseudo-first-order model, pseudo-second-order model, Elovich model, and intraparticle diffusion kinetic model.

The pseudo-first-order and pseudo-second-order models were given by

\[
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t
\]

(1)

where \( q_e \) (mg/g) is the adsorption capacity at equilibrium, \( q_t \) (mg/g) is the adsorption capacity at time \( t \) (min), and \( k_1 \) (1/min) and \( k_2 \) (g/(mg·min)) are the first- and second-order adsorption rate constants, respectively.

The Elovich equation was represented by the following equation

\[
q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t
\]

(3)

where \( \alpha \) (mg/(g·min)) and \( \beta \) (mg/g) are the adsorption constants.57

The Weber−Morris kinetic model of intraparticle diffusion was used in the following form

\[
q_t = k_1 t^{1/2}
\]

(4)

where \( k_1 \) (g/(mg min^{−1/2})) is the adsorption constant.58

The constant parameters of the four kinetic models are shown in Table 2 and Figure 4. The value of \( R^2 \) measured the goodness-of-fit test results fitting on the kinetic models. The
The acquired correlation coefficients of the four kinetic models were 0.851, 0.998, 0.968, and 0.896, respectively. The theoretical value of $q_e$ was closer to the experimental results, which was acquired through the pseudo-second-order model. The results showed that the adsorption process on RHAC was more in line with the pseudo-second-order model. This indicated that chemisorption played a dominant role.$^{59}$

**2.4. Isotherm Studies.** Adsorption isotherm was necessary to understand the adsorption mechanism. Meanwhile, it had a crucial role in determining the maximum adsorption capacity. The adsorption capacity of RHAC was determined using Langmuir and Freundlich isotherms.

The Langmuir isotherm model assumed that occurred within the sorbent specific uniform location. This model was given by the equation

$$
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}
$$

where $q_m$ is the maximum monolayer adsorption capacity (mg/g) and $K_L$ is the Langmuir constant (L/mg).

The separation coefficient ($R_L$) was used to prove whether the adsorption process was favorable and it was expressed as follows

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

Table 2. Kinetic Parameters for Hg(II) Adsorption on RHAC

| model             | parameter       | value  |
|-------------------|-----------------|--------|
| pseudo-first-order| $q_{e,exp}$ (mg/g) | 38.080 |
|                   | $q_e$ (mg/g)    | 37.048 |
|                   | $k_1$ (min$^{-1}$) | 0.006  |
|                   | $R^2$           | 0.851  |
| pseudo-second-order| $q_{e,exp}$ (mg/g) | 38.080 |
|                   | $q_e$ (mg/g)    | 44.843 |
|                   | $k_2$(g/(mg-min)) | 0.001  |
|                   | $R^2$           | 0.998  |
| Elovich model     | $\alpha$ (mg/(g-min)) | 5.396  |
|                   | $\beta$ (mg/g)  | 0.107  |
|                   | $R^2$           | 0.968  |
| intraparticle diffusion | $k_i$ (mg/(g-min$^{-1/2}$)) | 2.621  |
|                   | $R^2$           | 0.896  |

Figure 4. (a) Pseudo-first-order model, (b) pseudo-second-order model, (c) Elovich model, and (d) intraparticle diffusion model for Hg(II) adsorption on RHAC.
where \( C_0 \) is the highest initial concentration of the solute. The \( R_L \) value indicates whether the adsorption is unfavorable \((R_L > 1)\), linear \((R_L = 1)\), favorable \((0 < R_L < 1)\), or irreversible \((R_L = 0)\).\

Freundlich isotherm was a formula for describing nonuniform systems, represented as

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \( K_F \) (mg/g) is the Freundlich constant concerning the adsorption capacity and represents the intensity of adsorption.

The \( R^2 \) values of the Langmuir and Freundlich models obtained by linear fitting were 0.998 and 0.897, respectively, as shown in Figure 5 and Table 3. The \( q_m \) value obtained by the Langmuir model was 55.87 mg/g, which was close to the experimental result (53.70 mg/g). This illustrated that the Langmuir model better depicts the adsorption behavior of Hg(II) on RHAC. According to the \( K_L \) value fitted by the Langmuir model, the calculated \( R_L \) value was between 0 and 1.0 \((R_L = 0.021)\), which indicated that adsorption was favorable for the experiment. It could be inferred that the adsorption process of RHAC to Hg(II) could be regarded as homogeneous monolayer-layer adsorption, and there was no interaction between the adsorbed ions.

2.5. Regeneration of AC. The recyclability of activated carbon is of great significance to the measurement of economic efficiency; also, the regeneration performance of RHAC was much better than those in previous studies. Under acidic conditions, H\(^+\) ions replaced metal ions through ion exchange, thereby promoting the desorption of metal ions. Hydrochloric acid was often used to desorb metal ions from adsorbents in industrial production, and the cost was relatively low. As shown in Figure 6, the adsorption capacity of RHAC decreases from 38.08 to 25.40 mg/g. The results showed that the adsorbent still has excellent regeneration performance and strong adsorption capacity after five cycles. It has excellent potential for application in the treatment of mercury ion wastewater.

2.6. Comparison with Other Adsorbents. The adsorption capacity of various adsorbents to mercury ions was compared in detail. Generally speaking, the maximum adsorption capacity of activated carbon prepared from RH was satisfactory. The structural characteristics of various adsorbents, as well as the dosage and pH value of adsorbents under optimal adsorption conditions, are shown in Table 4. The adsorbents with large specific surface areas tend to have higher adsorption capacity. The best adsorption conditions were determined by the properties of adsorbent raw materials. Compared with other adsorbents, although the adsorption capacity of RHAC was not the highest, its main advantage was that it could be reused many times and there was a huge amount of raw materials.

3. CONCLUSIONS

The AC prepared from RH after two-stage heating was studied in this work. The specific surface area was 887.32 m\(^2\)/g and the total pore volume was 0.48 cm\(^3\)/g, respectively, indicating that

![Figure 5: (a) Langmuir isotherm model and (b) Freundlich isotherm model for Hg(II) adsorption on RHAC.](https://pubs.acs.org/journal/acsodf)

![Table 3: Langmuir and Freundlich Isotherm Constant Parameters](https://pubs.acs.org/journal/acsodf)

![Figure 6: Adsorption−desorption cycles of RHAC for Hg(II).](https://pubs.acs.org/journal/acsodf)
RHAC could effectively adsorb heavy-metal ions. FTIR and XPS characterizations showed that the oxygen-containing functional groups formed in RHAC due to the activation of KOH, which played an important role in the adsorption of mercury ions. The maximum adsorption capacity of RHAC was 55.87 mg/g, which was much higher than that of RHC. The experimental data obtained by the Langmuir model ($R^2 = 0.998$) and the pseudo-second-order kinetics model ($R^2 = 0.998$) presented a better fitting, which showed that the adsorption process was chemical adsorption of a single molecular layer. The adsorbent still has a high adsorption capacity after repeated adsorption–desorption cycles, indicating that the adsorbent possesses excellent reutilization ability. This work reported various advantages such as cheap materials, simple preparation method, and obvious removal effect, which opened up a new approach to treat heavy-metal-polluted wastewater.

### 4. MATERIALS AND METHODS

**4.1. Materials and Reagents.** Potassium hydroxide (90%, Shanghai Macklin Biochemical Co., Ltd.), sodium hydroxide (96%, Fuchen Chemical Reagents Co., Ltd.), sulfuric acid (95–98%, Guangzhou Chemical Reagent Factory), ethyl alcohol (99.7%, Tianjin Fuyu Fine Chemical Co., Ltd.), and hydrochloric acid (36–38%, Guangzhou Chemical Reagent Factory) were used. All of the above reagents were analytical reagent (AR) grade. RH was acquired from Acheng, Heilongjiang province, China.

**4.2. Preparation of Activated Carbon.** The RH was crushed into a powder and passed through an 80 mesh sieve, and then washed with distilled water to remove impurities. Removal of soluble organic matter was done by absolute ethyl alcohol soaking. The dried RH was mixed with 10% sulfuric acid and heated in a reaction kettle (HUASI Instrument Co., Ltd.) at 170 °C for 48 h. The carbonized product was heated in a tubular furnace (OTF-1200X, HF-kejing Material Technology Co., Ltd.) to 400 °C for 30 min, then heated to 850 °C for 1 h, and the product was rice husk carbon (RHC). The carbonization product was mixed with KOH (the mass ratio was 1–3) and heated in a tube furnace in argon: (i) the temperature was increased to 400 °C at the rate of 10 °C/min and maintained for 30 min and (ii) it continued to be heated to 850 °C at 10 °C/min and held for 1 h. The final product was RHAC. After grinding, RHAC and RHC were passed through a 100 mesh sieve, then washed with deionized water and absolute ethanol, and dried for subsequent use.

### 4.3. Characterization of Activated Carbon.**

The morphology of the prepared activated carbon was observed by scanning electron microscopy (SEM Hitachi, S-4800). The adsorbent was studied by N$_2$ adsorption and desorption isotherms at −196 °C using 3H-2000PS1 (Beishide Instrument Technology Co., Ltd.). Before performing gas adsorption measurements, AC was degassed under vacuum at 300 °C for 6 h. The BET method was used to calculate the specific surface area, while the BJH method was used to calculate the pore volume. FTIR spectra of RHAC for Hg(II) adsorption were recorded using a Shimadzu 8400S FTIR spectrometer (Shimadzu, Kyoto, Japan). The samples were mixed and ground with KBr as the background. Thin sheets were then prepared, which were finally analyzed in the region of 4000–500 cm$^{-1}$. XPS was performed to characterize the surface chemical composition of the adsorbent with an Al Kzr ray source by ESCALAB 250Xi (Thermo Fisher). The qualitative analysis of elements can be performed according to the position of the characteristic line spectrum appearing in the energy spectrum. The graphitization degree of the adsorbent was characterized by a Lab RAM HR800 Raman spectrometer (HORIBA Jobin Yvon, France) with an excitation wavelength of 785 nm. The zero-point charge ($\mathrm{pH_{pzc}}$) on the surface of the adsorbent was measured by a laser particle analyzer (nano ZS&Mastersizer 2000E) according to the following method: 0.01 g of adsorbent was mixed with 50 mL of deionized water, then adjusted to the desired pH with 0.10 M HCl or 0.10 M NaOH, and finally sonicated at 25 °C for 12 h.

**4.4. Hg(II) Removal Experiments.** Twenty milliliters of Hg standard solution (1000 mg/L of Hg(II) of HNO$_3$, 1.0 mol/L, from Macklin) was put in a 1 L volumetric flask with deionized water to obtain a 20.0 mg/L mercury ion stock solution. The static adsorption experiment was used to explore the change of adsorption capacity of the two adsorbents under the influence of various factors. The effects of different contact time (0–120 min), pH (2.0–6.0), adsorbent dosage (0.2–1.0 g/L), and initial concentration of Hg(II) (4–20 mg/L) on the adsorption capacity of RHC and RHAC were studied by a batch experiment. The effects of ionic strength were evaluated using potassium chloride and sodium chloride (0.01, 0.05, 0.10, 0.50, 1.00 M). A certain mass of adsorbent and 100 mL of mercury ion solution of specified concentration were put into a 150 mL conical flask for an adsorption experiment in a shaker (150 rpm) at 25 °C. The initial pH was regulated to the required value with a 0.10 M HCl or 0.10 M NaOH solution. After reaching the experimental setting time, the adsorbent was separated from the mercury ion solution; also, the liquid was collected for a concentration test. The concentration of mercury ions was determined by a liquid chromatography–atomic fluorescence spectrometer (LC-AFS 6500, HaiGuang Instrument Co., Ltd.).

The equilibrium adsorption capacity was defined as

$$q_e = \frac{(C_0 - C_e)}{m} \times V$$  

where $C_e$ and $C_0$ are the initial concentration of Hg(II) (mg/L) and the equilibrium concentration of Hg(II) (mg/L), $V$ is the volume of Hg(II) in the solution (L), and $m$ is the mass of the adsorbent (g).

**4.5. Desorption and Reuse of RHAC.** The desorption performance and regeneration ability of RHAC were explored. The tests were carried out as follows: RHAC (0.2 g/L) was mixed with an 8.0 mg/L Hg(II) solution. The mixture was
stirred at 150 rpm and a pH of 5.0 for 2 h. After that, the solid was filtered out and the desorption experiment was performed with 0.10 M HCl for 12 h at 150 rpm. Then, the RHAC was reused as a regenerant for five adsorption–desorption cycles.

4.6. Adsorption Kinetics. The kinetic model could predict the possible rate-control step, which was of great significance to explore the adsorption mechanism. Kinetic studies were performed using 0.02 g of RHAC, at pH 5.0, for different contact times (0–120 min).

4.7. Adsorption Isotherms. The effect of the adsorbent and the adsorbent was demonstrated by an adsorption isotherm. The usability of the isotherm models was explored and the adsorbent was demonstrated by an adsorption isotherm. The study was conducted by increasing the equilibrium concentration of Cd(II) at different pH values and collecting data at a constant temperature for each concentration.

4.8. Data Process. To reduce experimental errors, each experiment has been repeated three times. Each data point on the graph represents the average value of repeated calculations, and the error bars are the corresponding standard deviations.

AUTHOR INFORMATION

Corresponding Author
Yong Sun – College of Engineering, Northeast Agricultural University, Harbin 150030, P. R. China; Key Laboratory of Agricultural Renewable Resources Utilization Technology and Equipment in Cold Areas of Heilongjiang Province, Harbin 150030, P. R. China; Email: sunyong@neau.edu.cn

Authors
Zhiyuan Liu – College of Engineering, Northeast Agricultural University, Harbin 150030, P. R. China; CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Guangzhou 510640, P. R. China; Key Laboratory of Agricultural Renewable Resources Utilization Technology and Equipment in Cold Areas of Heilongjiang Province, Harbin 150030, P. R. China
Xinrui Xu – College of Engineering, Northeast Agricultural University, Harbin 150030, P. R. China; Key Laboratory of Agricultural Renewable Resources Utilization Technology and Equipment in Cold Areas of Heilongjiang Province, Harbin 150030, P. R. China
Jingbo Qu – College of Engineering, Northeast Agricultural University, Harbin 150030, P. R. China; Key Laboratory of Agricultural Renewable Resources Utilization Technology and Equipment in Cold Areas of Heilongjiang Province, Harbin 150030, P. R. China
Bin Qu – College of Engineering, Northeast Agricultural University, Harbin 150030, P. R. China; CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion, Guangzhou 510640, P. R. China; Key Laboratory of Agricultural Renewable Resources Utilization Technology and Equipment in Cold Areas of Heilongjiang Province, Harbin 150030, P. R. China; Email: orcid.org/0000-0002-0494-4872

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03992

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The authors declare no competing financial interest.

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