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Preparation of a quinoa straw-derived porous carbon material and a Fe$_3$O$_4$-contained composite material for removal of rhodamine B from water

Zhixiao Wang$^{1,2}$, Qinghua Zhou$^3$, Siji Chen$^1$, Dadong Liang$^3$, Shanshan Tang$^{1,*}$, Huan Chen$^1$, Guang Chen$^1,*$ and Bolun Zhang$^1$

$^1$ College of Life Sciences, The Key Laboratory of Straw Biology and Utilization, The Ministry of Education, Jilin Agricultural University, Changchun, Jilin 130118, People’s Republic of China

$^2$ The Basic Medical Department of Changchun Medical College, Changchun Medical College, Changchun, Jilin 130031, People’s Republic of China

$^3$ College of Resource and Environmental Science, Jilin Agricultural University, Changchun 130118, People’s Republic of China

* Authors to whom any correspondence should be addressed.

E-mail: tangshanshan81@163.com and chg61@163.com

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Abstract

In this work, quinoa straw (QS) is considered as a sustainable biomass resource to produce adsorbent materials for wastewater treatment. Two materials, a porous carbon material derived from QS (PCQS) and a Fe$_3$O$_4$-containing composite material based on the PCQS (Fe$_3$O$_4$@PCQS), were prepared. PCQS was prepared via carbonization and subsequent chemical activation of the QS using NaOH. Thereafter, PCQS was characterized by SEM, TEM, XRD, IR, XPS, and N$_2$ adsorption-desorption analysis. As a carbon material with heterogeneous pores, PCQS has a BET specific surface area of 3435.21 m$^2$ g$^{-1}$, which is about 175 times higher than that of the precursor QS (19.60 m$^2$ g$^{-1}$). The PCQS had an adsorption capacity of 1778.1 mg g$^{-1}$ toward rhodamine B (RhB), and the adsorption followed pseudo-second-order kinetics and the Freundlich isotherm model. The PCQS was further modified by synthesizing Fe$_3$O$_4$ magnetic nanoparticles on the surface of PCQS to give Fe$_3$O$_4$@PCQS. The adsorption capacity of Fe$_3$O$_4$@PCQS toward RhB reached 1156.2 mg g$^{-1}$, and it could be rapidly separated from water by applying an external magnetic field. The PCQS and Fe$_3$O$_4$@PCQS exhibited acceptable reusability which was evaluated through ten successive adsorption/desorption cycles. In summary, the adsorption capacities of PCQS and Fe$_3$O$_4$@PCQS toward RhB are comparable with most current adsorbents, including the graphene-based materials, which shows that QS is a promising biomass feedstock to prepare carbon-based materials and composites.

1. Introduction

Dyes are widely used in the production of various consumer products such as leathers, textile, paper, plastic, rubber, food, cosmetic, and so on [1, 2]. There are hundreds of thousands of tons of dyes produced annually [3, 4]. Inadequate treatment of wastewater containing residual dyes can be a significant source of severe environmental pollution. Some dyes are toxic and can be harmful to humans and aquatic lifeforms. Moreover, the presence of dyes in water interferes with the penetration of sunlight, decreases gas solubility, retards photosynthesis, and inhibits the growth of aquatic biota [5, 6].

To date, many efforts have been devoted to wastewater treatment. Adsorption is considered one of the best treatment methods because it is both highly efficient and easy to operate [7, 8]. Carbon-based materials are one of the best adsorbents due to their large surface area and strong interaction with various types of pollutants [9–11]. Cheap biomass wastes are an important raw material for the production of carbon-based materials. Various straw wastes, such as cotton straw [12], rice straw [13], corn straw [14], wheat straw [15], sorghum straw...
After the biomass waste is carbonized, the resulting char can be chemically activated to prepare porous carbon materials with a large surface area and high porosity. Frequently used chemical activators include alkali hydroxide \([31–33]\), \(\text{H}_3\text{PO}_4\) \([34, 35]\), \(\text{ZnCl}_2\) \([36]\), and so on \([37]\). Porous carbon materials derived from biomass waste using this process have shown good adsorption performances in wastewater treatment \([38]\). However, it is still desirable to find new sources of cheap biomass to produce porous carbon materials that have high dye adsorption capacities and can be easily separated, regenerated, and reused.

Quinoa \((\text{Chenopodium quinoa} \text{ Willd.})\) is native to the Andean region of South America and consumed as a staple food \([39]\). Nowadays, quinoa is cultivated worldwide because of the high nutritional value of quinoa seeds. However, the quinoa seeds make up only a small part of the mass of the whole quinoa plant, and the vast majority of the mass is made up of quinoa straw \((\text{QS})\). Consequently, large quantities of QS are produced as agricultural waste. Therefore, it is highly desirable to find ways of turning QS into a value-added product while also avoiding environmental pollution problems caused by carelessly discarding or burning QS.

Recently, we studied the preparation and dye adsorption performance of carbon materials derived from quinoa seed husks \((\text{QH})\) \([40]\). Compared to QH, QS makes up a much greater mass fraction of the whole plant. Yet QS has not been investigated as a potential raw material for producing functional materials. In our previous work, KOH was used as the chemical activator to enhance the surface area and porosity of the biomass char derived from QH. However, KOH is highly corrosive, and the use of a large number of KOH may damage...
devices used in wastewater treatment. Inadequate treatment of wastewater containing KOH may also pollute the environment. Moreover, rinsing the excess KOH from the samples can produce a lot of heat as the KOH dissolves, which is dangerous at the scale of industrial processes. Thus, here we replace KOH with the more environmentally friendly activator NaOH. Moreover, to regenerate an adsorbent material, the spent adsorbent must be thoroughly washed to completely remove the adsorbed dye molecules. This method consumes a lot of water and organic solvents, which increases the risk of polluting the environment. Thus, new and improved regeneration methods should be developed.

In this study, we prepared two QS-derived materials following Scheme 1 and evaluated their performances in adsorbing rhodamine B (RhB, figure S1 (available online at stacks.iop.org/MRX/7/125603/mmedia)), a representative dye, from aqueous solutions. The first material was a porous carbon material derived from QS (PCQS). After the QS was heated under an N₂ atmosphere, the QS biomass char (CQS) was obtained. CQS was then thoroughly mixed with NaOH and heated under N₂ to prepare the PCQS. The performance of PCQS was evaluated by adsorbing RhB from water. The kinetics and isotherms of the adsorption were investigated. The second material was a composite material (Fe₃O₄@PCQS) based on PCQS and Fe₃O₄. The Fe₃O₄ nanoparticles were incorporated onto the PCQS surface using the chemical coprecipitation method. The RhB adsorption capacity of Fe₃O₄@PCQS was also evaluated. The adsorbents were regenerated by thermal treatment under an N₂ atmosphere, and their reusability was investigated.

2. Materials and methods

2.1. Materials
All chemicals used in this work were analytical grade and used without further purification. HCl, NaOH, FeSO₄·7H₂O, FeCl₃·6H₂O, and NH₄H₂O were purchased from Beijing chemical plant (Beijing, China). RhB was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China). Deionized water was used in all the experimental processes.

2.2. Methods

2.2.1. Preparation of PCQS
QS was smashed and subsequently screened through metal sieves (80 to 100 mesh). The carbonization and activation processes were carried out in a horizontal tube furnace with an electrical heating system. QS was carbonized at 500 °C for 60 min under N₂ flow. The produced biochar, CQS, was mixed with NaOH by grinding the solids in an agate mortar at predetermined weight ratios (1:1 to 5:1) of NaOH to CQS. The CQS was activated by heating the mixture at a predetermined temperature (600 °C to 800 °C) for 60–90 min under N₂ flow. The mixture was washed with an aqueous HCl solution (0.1 mol l⁻¹) and deionized water until the pH value was neutral. The final product was dried at 80 °C for 12 h.

2.2.2. Preparation of Fe₃O₄@PCQS
The Fe₃O₄ nanoparticles on the surface of PCQS were prepared using the chemical coprecipitation method [41, 42]. In brief, PCQS (0.100 g) was stirred in an aqueous solution (30.00 ml) containing FeSO₄ (25.0 mmol l⁻¹) and FeCl₃ (50.0 mmol l⁻¹) under an N₂ atmosphere. NH₄H₂O (1.5 mol l⁻¹, 15.00 ml) was added dropwise, and the solution was stirred for 30 min. The resulting sample was collected with an adsorbent magnet and then washed with water. The product was vacuum dried at 80 °C for 12 h.

2.2.3. Characterization of adsorbents
Scanning electron microscope (SEM) images were taken on a SHIMADZU SSX-550 field emission scanning electron microscope (SHIMADZU, Co Ltd., Kyoto, Japan) operating at 10 kV under high vacuum. The samples were coated with thin gold layers prior to SEM observations. A transmission electron microscope (TEM; JEM-2100, 200 kV, JEOL Co. Ltd., Akishima, Tokyo, Japan) was used to investigate the dispersibility and particle sizes of Fe₃O₄ nanoparticles on the surface of PCQS. The sample was dispersed in ethanol using an ultrasonic cleaner. The resulting mixture was dropped on a carbon-coated Cu TEM grid and dried in air. The size distribution analysis of Fe₃O₄ nanoparticles dispersed on PCQS was performed using ImageJ and Origin softwares. Fourier transform infrared (IR) spectra were recorded in the wave number range of 400–4000 cm⁻¹ operating at room temperature under vacuum using a Bruker IFS 66 V/S spectrometer (Bruker Optics, Ettlingen, Germany). The samples prior to IR analysis were finely ground and mixed homogeneously with KBr at a ratio of about 1:100 (W/W). N₂ adsorption/desorption isotherms were carried out at 77 K under continuous adsorption conditions using a Micromeritics ASAP 2020 surface area and pore size analyzer (Micromeritics Inc., Norcross, GA, USA) with high purity nitrogen (99.9999%). Prior to gas adsorption measurements, the samples were degassed at 180 °C under vacuum for 12 h. The N₂ adsorption data were obtained in a relative pressure range of 10⁻³ to 0.99. The
surface area was calculated by the Brunauer Emmetttte Teller (BET) method while the total pore volumes were estimated from the amount adsorbed at a relative pressure of 0.99. Pore size distributions were derived from isotherms by the DFT method. Powder X-ray powder diffraction (XRD) analysis was carried out to identify crystallographic information in the samples using a Bruker D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with a Cu-Kα radiation source (λ = 0.15418 nm). The spectra were obtained at 40 mA with a voltage of 40 kV. The XRD patterns were recorded over the 2θ range of 4°–80° in step scan mode with a step size of 0.02° and a scan rate of 4° min⁻¹. The Raman measurements were performed using a Renishaw InVia Raman spectrometer (Renishaw, Wotton-under-Edge, Gloucestershire, UK) equipped with a 532 nm excitation laser over the wavenumber range of 1000–2000 cm⁻¹. The X-ray photoelectron spectroscopy (XPS) spectra were conducted using a Thermo ESCALAB 250 electron spectrometer (15 kV, 150 W; Thermo Fisher Scientific, Waltham, MA, USA) with a monochromatic Al Kα (h.c. = 1, 486.6 eV) X-ray source in ultrahigh vacuum (UHV; < 10⁻¹⁰ Torr), which was operated in the constant-pass mode. The binding energies of elements were calibrated according to the C1s peak of adventitious carbon (284.8 eV). The concentrations of RhB in aqueous solutions (λmax = 554 nm) were detected at room temperature using an Agilent Cary300 UV–vis spectrophotometer (Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a 1.0 cm quartz cell. The concentrations of RhB were calculated by the standard curve.

2.2.4. Reusability of adsorbents

The reusability of PCQS and Fe₃O₄@PCQS for removing RhB were investigated. In a typical process, the adsorbent (20.0 mg) was added to an aqueous RhB solution (100.00 ml, 100 mg l⁻¹) with a pH of 7 and stirred in the dark. After the equilibrium adsorption was achieved, the solid sample was separated from the solution. PCQS was separated through using a 0.22 μm filter membrane. Fe₃O₄@PCQS was separated by utilizing an adsorbent magnet. The recovered adsorbent was dried at 80 °C in air and then carbonized in a tube furnace at 500 °C for 60 min under N₂. The regenerated sample was then reused in the next adsorption experiment.

2.3. Batch adsorption experiments

The adsorbents were dried at 110 °C for 12 h under vacuum and stored in a desiccator until they were used. The adsorption experiments were carried out in a series of conical flasks (250 ml) containing RhB aqueous solutions (150.00 ml) with different initial dye concentrations (50 to 400 mg l⁻¹). The pH values (3, 5, 7, 9, and 11) of the RhB solutions were adjusted using aqueous HCl or NaOH solutions. In a typical experiment, the adsorbent was added to an RhB solution. Subsequently, the conical flask was shaken in a bath shaker at a speed of 150 rpm at 30 °C under air and in the dark. Samples (2.0 ml) were removed at pre-determined time intervals and then centrifuged. The concentration of RhB in the liquid supernatant was determined using a UV–vis spectrophotometer at the adsorption wavelength of RhB (554 nm).

The time and equilibrium adsorption capacities, qₜ and qₑ (mg g⁻¹), were calculated with equations (1) and (2), respectively.

\[
qₜ = \frac{(C₀ - Cₜ)V}{W} \quad (1)
\]

\[
qₑ = \frac{(C₀ - Cₑ)V}{W} \quad (2)
\]

where C₀, Cₜ, and Cₑ (mg l⁻¹) mean the initial, time, and equilibrium concentrations of RhB, respectively; V (L) and W (g) are the volume of the RhB solution and the weight of the adsorbent, respectively.

2.3.1. Adsorption kinetic models

In this work, three kinetic modes (pseudo-first order, pseudo-second order, and intra-particle diffusion models) were used to fit the experimental data.

Pseudo-first-order equation is the Kinetic model for describing the adsorption rate based on the adsorption capacity, and can be expressed by the following equation:

\[
\log (qₑ - qₜ) = \log qₑ - \frac{k₁}{2.303}t \quad (3)
\]

where qₑ and qₜ (mg g⁻¹) are the adsorption capacities at time t (min) and equilibrium, respectively; k₁ (min⁻¹) is the pseudo-first-order rate constant.

The pseudo-second order model is expressed as the equation (4).

\[
\frac{t}{qₜ} = \frac{1}{k₂qₑ²} + \frac{t}{qₑ} \quad (4)
\]

where k₂ (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant.
Intraparticle diffusion model was also employed to fit the experimental data. The model can be expressed by the equation (5).

$$q_t = k_i t^{0.5} + C$$

(5)

where $k_i$ (mg g$^{-1}$ min$^{-0.5}$) and $C$ (mg g$^{-1}$) are the diffusion rate constant within the particle and the constant associated with the thickness of the boundary layer, respectively.

2.3.2. Adsorption isotherms. Langmuir isotherm model may be expressed in equations (6) or (7).

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

(6)

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

(7)

Figure 1. SEM images of (a) QS, (b) CQS, (c) PCQS, and (d) Fe$_3$O$_4$@PCQS. TEM images of (e) Fe$_3$O$_4$@PCQS and (f) Fe$_3$O$_4$ nanoparticles dispersed on the surface of PCQS.
where \( q_e (\text{mg g}^{-1}) \) is the equilibrium adsorption capacity of adsorbent, \( q_m (\text{mg l}^{-1}) \) is the maximum adsorption capacity (\( \text{mg g}^{-1} \)), \( C_e \) is the equilibrium concentration of dye in solution, and \( K_L \) is the Langmuir constant (\( \text{l mg}^{-1} \)).

Freundlich isotherm model may be expressed in equations (8) or (9).

\[
q_e = K_F \cdot C_e^{1/n}
\]  
\[
\log q_e = \log K_F + \left( \frac{1}{n} \right) \log C_e
\]

where \( K_F \) is the Freundlich constant and heterogeneity factor, respectively.

3. Results and discussion

3.1. Characterization of adsorbents

QS was used as the raw material for preparing QS-based porous materials (Scheme 1). As shown in figure 1(a), QS had a smooth and non-porous surface. Its main components contain cellulose, hemicellulose, and lignin. QS was heated at 500 °C under N\(_2\). During the process of being heated in the absence of oxygen, the thermal depolymerization of lignocellulose happened, which resulted in the corresponding biomass char. Usually, the porosities of materials could not dramatically increase through pyrolysis [43–45]. As shown in figure 1(b), CQS had a smooth surface morphology similar to the QS precursor.

Chemical activation was frequently performed for creating more pores in the biomass char. Herein, NaOH was used as the activator. CQS was mixed with NaOH and heated to 700 °C under N\(_2\). The chemical reaction between NaOH and biomass carbon was suggested as follows [46]:

\[
6\text{NaOH} + 2\text{C} = 2\text{Na} + 2\text{Na}_2\text{CO}_3 + 3\text{H}_2
\]

SEM imaging showed exposed hollow channels and thin flaky walls in the PCQS (figure 1(c)). This change in morphology indicated that the surface of the CQS was successfully etched by reacting it with NaOH under the high temperature condition.

N\(_2\) adsorption-desorption analyses were carried out to further investigate the changes in the surface area and porosity.

\( S_{\text{BET}} (\text{m}^2 \text{~g}^{-1}) \) is the BET specific surface area, \( V_{\text{total}} (\text{cm}^3 \text{~g}^{-1}) \) is the total pore volume.

of the samples after the carbonization and chemical activation processes (figure 2, table 1, and figure S2). The BET method was used to analyse the structural characteristics of the samples. Raw QS exhibited a type III adsorption isotherm, which is characteristic of mesoporous materials. The pore size distribution ranged from 4 to 18 nm with a BET specific surface area of 19.60 m\(^2\) g\(^{-1}\). After the carbonization process, the resulting CQS had a similar N\(_2\) adsorption isotherm, pore size distribution, and BET specific surface area compared with that of the QS. The CQS adsorption isotherm was type III. The pore size distribution in the CQS also ranged from 4 to 18 nm and the BET specific surface area was 31.25 m\(^2\) g\(^{-1}\). However, the PCQS formed by further chemical activation of the CQS had a type IV adsorption isotherm. A type IV adsorption isotherm is indicative of the presence of both micropores and mesopores in the material [47]. The pore size distribution of the PCQS ranged from 0.5–2.1 nm and 2.2–8.0 nm, with an average pore diameter of 2.43 nm. The BET specific surface area of PCQS was 3435.21 m\(^2\) g\(^{-1}\) which was approximately 110 times and 175 times higher than the CQS and QS.
precursors, respectively. Moreover, the total pore volume of PCQS was 2.091 cm$^3$ g$^{-1}$ which was approximately 38 times and 20 times higher than that of the CQS (0.0550 cm$^3$ g$^{-1}$) and QS (0.1028 cm$^3$ g$^{-1}$), respectively. These results demonstrated that the PCQS was a material with a large surface area and high porosity. Comparing the three materials suggests that all of the micropores and the majority of the mesopores were formed during the chemical activation process rather than carbonization process. Moreover, NaOH was a highly effective activator that could be used to create both micropores and mesopores in CQS.

In the Raman spectra of QS, CQS and PCQS were shown in figure 3(a). There were two characteristic bands in the range of 1000–2000 cm$^{-1}$. The band at 1600 cm$^{-1}$, is usually referred to as the graphitic (G) band. The G band represents the in-plane vibrations of the carbons in the graphitic structure. The other band at 1350 cm$^{-1}$, is referred to as the disordered (D) band. The presence of the D band indicates that there are poorly ordered carbon atoms present in the sample [48]. The above Raman results indicated that QS, CQS, and PCQS were composed of graphitic carbon and amorphous carbon. However, there were differences in the degree of graphitization. The relative intensity ratio of the D band and G band (I_D/I_G) for the QS was 0.78. After carbonization, the I_D/I_G value of CQS changed to 0.68, and the change could be resulted from the thermal

| Samples  | $S_{BET}$ (m$^2$ g$^{-1}$) | $V_{total}$ (cm$^3$ g$^{-1}$) |
|----------|---------------------------|-----------------------------|
| QS       | 19.60                     | 0.1028                      |
| CQS      | 31.25                     | 0.0550                      |
| PCQS     | 3435.21                   | 2.091                       |
| Fe$_3$O$_4$@PCQS | 3175.77                  | 1.739                       |

Figure 4. (a) C1s and (b) O1s high resolution spectra of PCQS.

Figure 3. (a) Raman spectra of QS, CQS, and PCQS. (b) IR spectra of QS, CQS, and PCQS.
decomposition of lignocellulose. After chemical activation, the I_D/I_G value of CQS further changed to 0.92, which could be resulted from the reaction of NaOH with CQS.

The IR spectra of the QS, QSC, and PCQS are shown in figure 3(b). The IR spectrum of the QS was similar to other biomass materials composed of cellulose, hemicellulose, and lignin. The peaks at 3357, 2921, 1738, 1634, and 1054 cm\(^{-1}\) were assigned to the –OH, C–H, C=O, C=C, and C–O groups, respectively. In the IR patterns of the CQS and PCQS, some of the peaks were weaker than in the QS, which suggested that some of the functional groups decomposed during the carbonization and activation processes [49, 50].

The surface chemical composition of the PCQS was characterized by XPS (figure 4). The high-resolution C1s spectrum of PCQS could be divided into three individual component peaks corresponding to C–C (284.6 eV), C–O–C (285.2 eV), and C–O (286.8 eV). The O1s high-resolution spectrum of PCQS could be divided into two different oxygen-containing groups: C–O (532.8 eV) and -OH (533.4 eV) [51, 52]. These XPS results are in good agreement with the IR data.

In addition to the PCQS, a composite material derived from QS was also prepared (Scheme 1). Through the treatment of PCQS with solutions containing Fe\(^{3+}\), Fe\(^{2+}\), and NH\(_3\), Fe\(_3\)O\(_4\) nanoparticles were synthesized on the surface of PCQS. As shown in figures 1(d)–(f), the Fe\(_3\)O\(_4\) particles were homogeneously dispersed on the surface of PCQS. The Fe\(_3\)O\(_4\) particle sizes ranged from 9 to 33 nm (figure S3).

As shown in figure 5(a), the N\(_2\) adsorption isotherm of Fe\(_3\)O\(_4\)@PCQS was lower than that of PCQS, as was its BET surface area of 3175.77 m\(^2\) g\(^{-1}\) compared to 3435.21 m\(^2\) g\(^{-1}\) for PCQS. The total pore volume of the Fe\(_3\)O\(_4\)@PCQS was 1.739 cm\(^3\) g\(^{-1}\) which was also lower than that of PCQS (2.091 cm\(^3\) g\(^{-1}\)) (table 1). Also, there were some changes in the pore size distributions between the PCQS and Fe\(_3\)O\(_4\)@PCQS (figure 5(b)). These changes may have been due to the introduction of Fe\(_3\)O\(_4\) nanoparticles on the surface of PCQS. All the characteristic peaks in the IR spectra (figure 6(a)) of Fe\(_3\)O\(_4\)@PCQS could be assigned to either Fe\(_3\)O\(_4\) or PCQS. There were some additional peaks in the XRD pattern of Fe\(_3\)O\(_4\)@PCQS compared to PCQS (figure 6(b)). The
positions of these additional diffraction peaks were in good agreement with the peaks expected for Fe₃O₄ prepared through the chemical coprecipitation method and pure Fe₃O₄ (JCPDS card no. 19–0629) [53–55]. Together, the characterization of the composite material above demonstrated that the sample was composed of both Fe₃O₄ and PCQS. The results demonstrated that the chemical coprecipitation method was an effective means for preparing a composite material containing Fe₃O₄ nanoparticles and porous carbon materials.

3.2. Preparation of materials

3.2.1. Preparation of PCQS

In PCQS, all of the micropores and most of the mesopores were created through the etching of CQS with NaOH. Usually, the activation temperature, activation time, and the alkali/carbon ratio are key activation conditions which strongly influence the degree of chemical etching [56–58]. The porous carbon materials with different degree of chemical etching may exhibit different dye adsorption capacities. Lower degree of chemical etching leads to relatively lower dye adsorption capacity. The optimal degree of chemical etching leads to the highest dye adsorption capacity. Excessive degree of chemical etching may lead to the collapse of pores resulting relatively lower dye adsorption capacity. In other words, the highest dye adsorption capacities could be used as a key indicator for confirming the best activation conditions.

A series of experiments were performed to investigate the effects of the activation temperature, the activation time, and the ratio of NaOH and CQS on the RhB adsorption capacities of the resulting PCQS (figure 7 and table S1). The best activation conditions were determined on the basis of the highest RhB adsorption capacities of samples.

The effect of the activation temperature on the RhB adsorption capacity of PCQS was investigated. The reaction time and alkali/carbon ratio were 60 min and 4:1, respectively. When the activation temperature was increased from 600 °C to 700 °C, the RhB adsorption capacity of PCQS increased from 764.5 to 1778.1 mg g⁻¹ (figure 7(a)). However, when the temperature was further increased to 800 °C, the RhB adsorption capacity of
samples gradually decreased to 1162.3 mg g$^{-1}$, suggesting that too high of a reaction temperature resulted in excessive etching of the biomass char. Thus, the optimum activation temperature was determined to be 700 °C.

The effect of the activation reaction time on the adsorption capacity of PCQS was also investigated. The activation temperature and alkali/carbon ratio were 700 °C and 4:1, respectively. As shown in figure 7(b), the RhB adsorption capacities of samples changed with varying reaction time. When the activation time increased from 30 min to 60 min, the RhB adsorption capacity increased from 904.2 to 1778.1 mg g$^{-1}$. However, when the activation time was further increased to 90 min, the adsorption capacity of sample decreased to 1200.3 mg g$^{-1}$, which suggests that the phenomenon of excessive etching happened. Therefore, the best activation time was found to be 60 min.

![Figure 9](image_url) (a) Effect of pH on adsorption capacities of PCQS to RhB and (b) zeta potentials of PCQS.

![Figure 10](image_url) (a) Effect of contact time and initial RhB concentration on adsorption of RhB by PCQS ($V = 150$ ml, adsorbent dosage = 0.067 g l$^{-1}$, and pH = 7). Plots of (b) pseudo-first-order, (c) pseudo-second-order, and (d) intra-particle diffusion kinetic models.
Figure 7(c) shows the effect of alkali/carbon ratio on the adsorption capacity of the PCQS. The experiments were carried at 700 °C for 60 min based on the optimized conditions above. The RhB adsorption capacities of samples first increased and then decreased with increasing alkali/carbon ratios, suggesting that there was also an optimum amount of chemical activator. When the alkali/carbon ratios were 1:1, 2:1, 3:1, 4:1, and 5:1, the adsorption capacities were found to be 400.2, 700.1, 1077.4, 1778.1, and 950.15 mg g\(^{-1}\), respectively. Thus, the optimum alkali/carbon ratio was determined to be 4:1.

In summary, the investigations of the reaction conditions above suggested that the optimum CQS activation conditions were 700 °C for 60 min with an alkali/carbon ratio of 4:1. The conditions resulted in PCQS materials that exhibited a higher RhB adsorption capacity than samples activated at other conditions.

3.2.2. Preparation of Fe\(_3\)O\(_4@\)PCQS
Magnetic Fe\(_3\)O\(_4\) nanoparticles were introduced onto the surface of PCQS to facilitate rapid and efficient recovery of the adsorbent. As shown in the figure 8, the recovery rate of the adsorbent increased with increasing concentrations of Fe\(^{2+}\) and Fe\(^{3+}\) in the sample. However, the increase in Fe\(^{3+}\) and Fe\(^{3+}\) concentration also decreased the adsorption capacity of the composite. As a result, the concentrations of Fe\(^{2+}\) and Fe\(^{3+}\) were controlled to 25.0 and 50.0 mmol l\(^{-1}\), respectively, when preparing composites based on 100 mg of PCQS. The Fe\(_3\)O\(_4@\)PCQS prepared using the conditions above had an RhB adsorption capacity of 1156.2 mg g\(^{-1}\) in a solution with an initial dye concentration of 400 mg l\(^{-1}\). In one minute, 90.1% of the adsorbent was recovered.

3.3. Adsorption of RhB onto PCQS
3.3.1. Effect of pH on adsorption
The pH values of the dye solutions can also influence the performance of adsorbent materials by changing their surface properties. Herein, the adsorption performance of PCQS toward RhB was explored as a function of dye solution pH, shown in figure 9(a). When the pH value of the RhB aqueous solutions increased from 3 to 7, the adsorption capacities increased from 1283.4 mg g\(^{-1}\) to 1778.1 mg g\(^{-1}\). However, no obvious changes in RhB adsorption capacities were observed at pH values of 9 or 11. As a result, the pH value of 7 was selected as the optimum condition for adsorption experiments. Zeta potential measurements were used to determine the surface charge of PCQS materials with changing pH. As shown in figure 9(b), the zeta potentials of the PCQS are negative over the pH range of 3–11. Therefore, the negatively charged adsorbent could electrostatically interact with the positively charged RhB dye.

3.3.2. Adsorption kinetics
The adsorption properties of PCQS were studied by removing RhB from simulated wastewater. Figure 10(a) shows the measured RhB adsorption capacities as a function of contact time. When the initial dye concentration increased from 50 mg l\(^{-1}\) to 250 mg l\(^{-1}\), the adsorption capacity gradually increased. The higher initial concentration provided a greater driving force for the RhB molecules to overcome the mass transfer resistance between the aqueous phase and carbon-based adsorbent. Thus, more active sites and pores on the PCQS were occupied by RhB molecules resulting in a higher adsorption capacity.

PCQS could rapidly adsorb RhB from the aqueous solution. In the first 5 min, the adsorption capacities of PCQS reached 197.21, 399.92, 508.24, 651.40, and 807.92 mg g\(^{-1}\), respectively, for RhB solutions with initial concentrations of 50, 100, 150, 200, and 250 mg l\(^{-1}\). This rapid adsorption may be due to the large surface area
and high porosity of the PCQS (Figure 5). There are a large number of adsorption active sites and pores on the surface of PCQS, and they may not all be occupied by dye molecules after the initial adsorption processes.

The amount of RhB adsorbed by PCQS further increased with increasing contact time. However, when the contact time exceeded 60 min, additional dye adsorption was limited. This saturation likely resulted from the dramatic decrease in the available adsorption sites and pores with increasing contact time. From 90 to 120 min, the changes in adsorption plateaued, which suggested that the adsorption had equilibrated after 120 min of contact time.

The adsorption kinetics were investigated using pseudo-first-order and pseudo-second-order models [59, 60]. The kinetic model parameters are listed in Table 2. Initially, the experimental data were fit to a pseudo-first-order equation. The linear plots of $\ln(q_t - q_e)$ versus $t$ for different concentrations of RhB adsorbed on PCQS at 30 °C are presented in Figure 10(b). The values of $k_1$ and $q_{e, cal}$ were calculated from the fit slope and intercept, respectively. The $R^2$ values for the fits ranged from 0.8519–0.9139. The values of $q_e$ calculated from the pseudo-first-order model ranged from 192.5–448.7 mg g$^{-1}$, while the $q_e$ values obtained from the experimental results ranged from 320.7–1109.4 mg g$^{-1}$ for initial dye concentrations of 50 mg l$^{-1}$ to 250 mg l$^{-1}$. There were

| Table 2. Kinetic models parameters of RhB adsorption onto PCQS. |
|----------------------|----------------------|----------------------|
| $C_0$ (mg l$^{-1}$)  | $q_{e, exp}$ (mg g$^{-1}$) | $k_1$ (min$^{-1}$) | $q_{e, cal}$ (mg g$^{-1}$) | $R^2$ |
| 50                  | 320.7                | 0.052716            | 192.5               | 0.9139 | 0.000781 | 329.0         | 0.9978 |
| 100                 | 539.1                | 0.058588            | 226.2               | 0.8519 | 0.00994  | 543.5         | 0.9992 |
| 150                 | 758.1                | 0.041638            | 293.2               | 0.7202 | 0.000414 | 793.7         | 0.9993 |
| 200                 | 937.8                | 0.071186            | 311.3               | 0.8719 | 0.000362 | 980.4         | 0.9995 |
| 250                 | 1109.4               | 0.05792             | 448.7               | 0.8563 | 0.000381 | 1165.5        | 0.9998 |

| Table 3. Adsorption isotherms parameters of RhB on PCQS and Fe₃O₄@PCQS. |
|----------------------|---------------------|---------------------|
| Adsorption isotherms | Constants           |
| PCQS Langmuir        | $q_m$ (mg g$^{-1}$) | $K_L$               | $R^2$ |
|                      | 2157.03             | 0.005918            | 0.9783 |
| Freundlich $K_f$     | n                   | $R^2$               |
|                      | 26.14               | 1.3619              | 0.9911 |
| Fe₃O₄@PCQS Langmuir  | $q_m$ (mg g$^{-1}$) | $K_L$               | $R^2$ |
|                      | 1428.57             | 0.007511            | 0.9714 |
| Freundlich $K_f$     | n                   | $R^2$               |
|                      | 31.22               | 1.5803              | 0.9903 |

Figure 12. The RhB adsorption capacities of PCQS and Fe₃O₄@PCQS under different initial concentrations ($V = 150$ ml, adsorbent dosage = 0.067 g l$^{-1}$, and pH = 7).
significant differences between the calculated and experimental values of \( q_e \), which suggested that the adsorption processes did not follow a pseudo-first-order kinetic model.

Thus, the experimental data were also fit with the pseudo-second-order kinetic model. The calculated values of \( q_{e,\text{cal}} \) (329.0–1165.5 mg g\(^{-1}\)) were in better agreement with the corresponding experimental data (320.7–1109.4 mg g\(^{-1}\)). The \( R^2 \) values ranged from 0.9978–0.9998. The high \( R^2 \) values supported that the \( t/qt \) and \( t \) were linear and that the adsorption followed a pseudo-second-order kinetic process rather than a pseudo-first-order diffusion model.

Moreover, the data were also fit using the intra-particle diffusion model. As shown in figure 10, the adsorption of RhB onto the adsorbent may be governed by different stages. Within the first 10 min, the adsorption process represented external mass transfer and rapid adsorption of RhB molecules onto the outer surface of the adsorbent. The following linear stage represented the intra-particle process where the dye molecules migrated into the pores and were adsorbed on the inner surface of the adsorbent [8].

3.3.3. Adsorption isotherms

The adsorption experiments of PCQS toward RhB at 303 K were also analysed with two typical isotherm models (the Langmuir and Freundlich models) as shown in figure 11(a) and S4. The data were poorly fit with the Langmuir model with an \( R^2 \) of 0.9783, and were better fit with the Freundlich model with an \( R^2 \) of 0.9911 (table 3). Thus, the adsorption data were fit with the Freundlich model, which suggested that the RhB ions were adsorbed onto the heterogeneous sites of the adsorbent. The value of \( 1/n \) was less than 1, which was indicative of a favourable adsorption isotherm [11]. The equilibrium adsorption capacity reached 1778.1 mg g\(^{-1}\) for an initial RhB concentration of 400 mg l\(^{-1}\), which was comparable with most reported adsorbents including the biochars, porous materials, and graphene-based materials (table S3).

As shown in figure 12, the RhB adsorption capacities were in the range of 280.66–1156.2 mg g\(^{-1}\) when the initial concentration of RhB were in the range of 50–400 mg l\(^{-1}\). Through comparing the adsorption performance of Fe\(_3\)O\(_4@\)PCQS with that of PCQS, it can be seen that the introduction of Fe\(_3\)O\(_4\) decreased the dye adsorption capacities. Typically, when the initial concentration of RhB was 400 mg l\(^{-1}\), the adsorption capacity of Fe\(_3\)O\(_4@\)PCQS reached 1156.2 mg g\(^{-1}\) which is lower than that of PCQS (1778.1 mg g\(^{-1}\)). The Langmuir and Freundlich models were used to fit the data of dye (figures 11(b) and S5). As shown in table 3, the data were better fit the Freundlich model (\( R^2 = 0.9903 \)) and were poorly fit with the Langmuir model (\( R^2 = 0.9714 \)), which is in agreement with case of PCQS.

3.3.4. Reusability of PCQS and Fe\(_3\)O\(_4@\)PCQS

To meet the demands for low-cost wastewater treatment, good regeneration performances are highly desirable in adsorbents. The reusability of both the PCQS and Fe\(_3\)O\(_4@\)PCQS were evaluated through ten successive adsorption/desorption cycles (figure 13). After the recovered adsorbent was thermally treated, the adsorbed RhB was carbonized, and the adsorbent was reused. During the successive cycles, the performance decreased slightly, which may suggest that the available active sites and pores on the surface of adsorbents were progressively more occupied after each cycle. Nevertheless, the PCQS and Fe\(_3\)O\(_4@\)PCQS maintained 78% and 67% of their initial adsorption capacities after ten cycles, respectively. These results indicated that both PCQS
and Fe₃O₄@PCQS had good recyclability and economic potential. However, compared with PCQS, the composite Fe₃O₄@PCQS could be more conveniently, simply, and rapidly recovered from the water phase, which make it favourable for potential industrial applications. Fe₃O₄@PCQS could be rapidly separated from the water phase using magnets (figure S6). After one minute, the Fe₃O₄@PCQS recovery reached about 90% and reached 98% after three minutes.

4. Conclusion

Herein, a porous carbon material and a composite material were prepared using QS as the raw material. After the QS was carbonized and chemically activated, the produced PCQS had abundant and heterogeneous pores. The PCQS specific surface area (3435.21 m² g⁻¹) and total pore volume (2.091 cm³ g⁻¹) were approximately 175 times and 38 times higher than those (31.25 m² g⁻¹ and 0.0550 cm³ g⁻¹) of the precursor CQ5S, respectively. The RhB adsorption capacity of the PCQS reached 1778.1 mg g⁻¹. Moreover, the Fe₃O₄@PCQS composite also had a good RhB adsorption capacity (1156.2 mg g⁻¹). It could be rapidly separated from water phase, and exhibited acceptable reusability after 10 cycles. In summary, QS was shown to be a promising biomass feedstock for producing carbon materials and composite materials. The conversion of QS to value-added products is potentially helpful for reducing pollution caused by inadequate treatment of current QS agricultural waste. The activation conditions explored in this work may be amenable to industrial scale production of adsorbent materials. In future works, we will continue to design and prepare more composites based on QS for use in applications such as controlled release, catalysis, and supercapacitors.

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ORCID iDs

ShanshanTang https://orcid.org/0000-0002-7212-0402

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