Resource Utilization of Agricultural Residues: One-Step Preparation of Biochar Derived From Pennisetum Giganteum For Efficiently Removing Chromium From Water In A Wide pH Range

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Resource utilization of agricultural residues: One-step preparation of biochar derived from *Pennisetum giganteum* for efficiently removing chromium from water in a wide pH range

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Abstract: Biochars derived from agricultural residues, *Pennisetum giganteum*, were prepared by a one-step activation method after impregnated with H$_3$PO$_4$. The effects of activation temperature and H$_3$PO$_4$ impregnation method on the structure and performance of biochar were investigated. Characterizations such as XPS, FTIR, and N$_2$ adsorption-desorption curves showed that the P-containing biochar prepared by one-step method had a large specific surface area, large pores, and abundant surface functional groups. And, C-P, O-P, C-O, and other groups participated in the adsorption and removal of Cr(VI). Moreover, the target adsorbent has a good effect on Cr removal in a wide range of pH (the removal rate was more than 55.92%, at pH $\leq$ 9). Interestingly, the changing trend of pH value in the reaction process under different initial pH values proved that the adsorbent itself could regulate the pH of the external environment.

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solution by providing acid groups, thus keeping the adsorption equilibrium solution in a narrow pH range. In addition, the target adsorbent had excellently selective adsorption capacity and good removal capacity (≥77.4%) after five times of reuse. This work should permit for providing a convenient utilization of *Pennisetum giganteum* agricultural residues and confirmed that the biochar treated with H$_3$PO$_4$ can remove chromium in a wider pH range through self-regulation.

**Keywords:** Agricultural residues; H$_3$PO$_4$-treated biochar; pH range; Cr(VI); Selective adsorption

1. **Introduction**

Chromium (Cr) is a toxic heavy metal that constitutes a seriously threat to human health (Santiago et al. 2010). Chromium is derived from a wide range of sources, including electroplating, leather, printing and dyeing, metallurgy among others (Xin et al. 2018). In an aquatic environment, chromium primarily exists in two stable oxidation states: Cr (III) and Cr (VI). Cr (VI) has high mobility in the aquatic system and is about 500 times more toxic than Cr (III) (Jiang et al. 2015). Cr (VI) is carcinogenic (causing lung cancer), causes dermatitis, renal circulation, and other serious diseases. The US EPA regulated the Cr (VI) concentration standards as <0.1 mg L$^{-1}$ for natural waters and...
<0.05 mg L⁻¹ of drinking water (Onchoke & Sasu 2016). Therefore, the treatment of Cr
(VI) pollutants was of importance to public health and environmental protection. Several
methods, including chemical precipitation, electrocoagulation, electrochemical
treatment, reverse osmosis, membrane filtration or ion exchange and adsorption, have
been employed to remove Cr (VI) from aqueous solutions (Ankur & Chandrajit 2016;
Ramavandi et al. 2014; Zhao et al. 2017). Among these methods, adsorption technique
was considered as an efficient and attractive method owing to its effectiveness,
simplicity, and cheapness (Jiang et al. 2018). At present, a variety of adsorbents (such as
biochar, polymer, gel, natural, and waste) were reported to be used as clay minerals for
the treatment of polluting wastewater (Sophia & Lima 2018). Biochar, a relatively
new adsorbent, that has attracted increasing attention on account of its rich and
renewable properties in raw materials and the characteristics of "treating waste with
waste" (Singh et al. 2019; Tong et al. 2019). Because of its rich surface functional groups,
large porosity and ability to reduce carbon emissions, biochar be used as a cheap
carbon material adsorbent and can meet the requirements of low-cost adsorbent to
remove heavy metals, and can be used to treat industrial wastewater. (Chao et al. 2015;
Kong et al. 2014). The removal of metal ion by biochar is the result of a variety of
mechanisms, including precipitation, complexation, ion exchange, electrostatic
adsorption and physical adsorption (Dong et al. 2011a). Specific ligands and functional
groups, such as -OH and -COOH on the surface of biochar can form complexes or
precipitates with heavy metals (Mahdavi et al. 2013), which belonged to chemical
adsorption. However, physical adsorption mainly depended on the surface properties of
biochar, such as specific surface area and pore structure (Sigmund et al. 2017). Most
studies showed that it was impossible to become an important mechanism for heavy
metal adsorption. The surface charge of biochar adsorbs metal ions with an opposite charge through electrostatic interaction, which is one of the main mechanisms of removing heavy metal ions by biochar. For example, biochar prepared at high temperature (>400 °C) is easy to form a graphene structure, which further improves the electrostatic adsorption capacity of biochar and heavy metals (Wang 2018).

Generally, the adsorption mechanism of metal ions by biochar prepared by different activators is quite different. The common activators are ZnCl₂, KOH, Na₂CO₃, H₃PO₄, etc. Yang et al. (Li et al. 2020). Researchers (Yu et al. 2020) used FeCl₃ and ZnCl₂ modified corn straw to remove Cr (VI), and its adsorption capacity could reach 138.89 mg g⁻¹, but the solution environment had to be adjusted to pH = 2. The addition of polyethyleneimine and phosphorus increased the number of active centers of the biochar from the oil tea shell, and the adsorption capacity reached 355 mg g⁻¹ (Chen et al. 2018).

For the materials reported in the literature, the pH value of the solution usually should be adjusted to acidic conditions (usually pH<3), which was confined within a narrow range (Sigmund et al. 2017; Xin et al. 2018). Therefore, the development of new biochar adsorbents with low cost and large pH range is still the sustainable goal of environmental remediation. However, in the past, studies focused on how to improve the adsorption capacity of the adsorbent (Ahmadi et al. 2016), and few researchers paid attention to how to modify the adsorbent to make the adsorbent have better chromium removal effect in a wide range of pH.

Herein, a new type of H₃PO₄-porous carbon was prepared by direct pyrolysis Pennisetum giganteum, which was earlier impregnated with phosphoric acid. Homogeneous carbonized biomass materials were prepared by one-step carbonization activation at a lower temperature. The adsorption isotherm and kinetic model were
analyzed and the stability of P-pg BC was tested. The results showed that phosphoric acid activated biochar can self-regulate the pH of the system. By providing protons, the pH of the initial solution was finally maintained in a narrow pH range. The purpose of this study is to synthesize biochar with sufficient surface acidity, which can remove chromium in a wide range of pH, to reveal the relationship between surface groups and adsorption properties of biochar.

2. Material and method

2.1 Materials and Reagents

Pennisetum giganteum was kindly provided by Kunming Hengfa Technology Co., Ltd, Yunnan, China. Sodium hydroxide (NaOH), phosphoric acid (≥ 85.0%), acetone (≥ 99.0%), furfural (≥ 99.5%), sulfuric acid (≥ 98%), potassium dichromate (≥ 99.9%), and the other AR reagents were purchased from Shanghai McLean Biochemical Technology Co., Ltd. Deionized water was used to prepare all solutions and all the experimental steps. All chemicals used in this study were of commercially available analytical grade and used without further purification.

2.2 Preparation of activated carbon from Pennisetum giganteum (P-pgBC)

First of all, the Pennisetum giganteum stem should be washed and dried overnight in the oven. The dried Pennisetum giganteum was crushed with a grinder, screened through a 40-60 mesh sieve, and packed in plastic bags for standby (named as raw material). And then, there were two kinds of activation methods: one was that the raw materials were pre-carbonized, and then the pre-carbonized carbon was mixed with a certain proportion of phosphoric acid (1:1, 1:2, 1:3), and then activated directly in the N₂ atmosphere at target temperature (labeled as Yp-pgBC-X °C), the other was mix the raw
material with phosphoric acid in a certain proportion (1:1, 1:3), immersed it in an oven at 60 °C for 24 h, and then activated it in N₂ atmosphere at target temperature (labeled as Zp-pgBC-X °C). Among them, the condition of pre-carbonization refered to that carbonization in nitrogen atomosphere at 400 °C for 2 h in a tube furnace. The activation temperature was between 300 °C and 500 °C, the rate was 5K/min, and the time was 1 h. The materials prepared by the two methods were washed to neutral with deionized water and then dried in the oven overnight. Grind the dried materials and put them into plastic bags for standby. At this point, the adsorbent was ready.

2.3 Characterization

S\textsubscript{BET} and pore size of Z\textsubscript{p}-pgBC-400 °C were completed by Brunauer-Emmett-Teller and Barrett-Joiner-Halenda method. The phase structure of Z\textsubscript{p}-pgBC-400 °C was obtained via an X-ray diffractometer (XRD, PANalytical). Surface element composition and element valence analysis also were examined by X-ray photoelectron spectroscopy (XPS, Thermo fisher Scientific K-Alpha⁺). Fourier transforms infrared (FTIR) spectra were recorded on an FTIR Spectrophotometer in the range of 4000–500 cm\textsuperscript{-1} using KBr pellet. SEM and EDS were performed by field emission scanning electron microscope (Sigma model, Zeiss, Germany).

2.4 Batch Cr(VI) adsorption experiments

The typical adsorption process is as follows: 50 mL Cr(VI) solution (10-100 mg/L) and required weight of adsorbent (0.5-2.0 g/L) were added in a 150 ml conical flask for a batch experiment. Also, the effects of pH (1-9), contact time (0-24 h), and temperature (25, 40, and 55 °C) on Cr (VI) adsorption efficiency were also studied. And all speeds of the reciprocating shaker were set to 160 rpm. The pH of the solution was adjusted with 0.1 M NaOH and 0.1M HCl. After 24 h, The concentration of remaining Cr(VI) anions
in the adsorption medium was determined at 540 nm using a double beam UV-VIS spectrophotometer after complexation with 1,5 diphenylcarbazide. To ensure the accuracy, reliability, and reproducibility of the data, all the batch experiments were carried out in triplicate for statistical purposes and the adsorption capacities were calculated by the following equation:

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]  
\[ q = \frac{(C_0 - C)}{m} \times V \]

Where \( C_0 \) and \( C \) (mg/L) are the initial and equilibrium concentrations of Cr(VI), \( m \) is the mass of absorbent (g), and \( V \) (L) is the volume of solution.

3. Results and Discussion

3.1 Optimization of Activation Conditions

Before the formal experiment, a large number of pre experiments were carried out, and the best adsorption materials were selected. Firstly, the carbon materials prepared by KOH two-step activation method reported by our research group were tested. It was found that it took long time for the adsorption to reach equilibrium, and the high removal efficiency could be only under acidic conditions. Therefore, five kinds of carbon materials were prepared by using phosphoric acid as an activator and their removal effects were tested. And, the concentration of Cr(VI) was 50 mg/L, the reaction temperature was 25 °C, and the amount of adsorbent was 0.1 g. The chromium solution used was the natural pH value.

According to Table S1, the biochar prepared via one-step method has a good removal effect on Cr(VI), and the optimal mass ratio of carbon to phosphorus is 1:3. Next, the effects of activation temperature on the surface area, pore volume, and
removal efficiency of porous carbon materials were studied. The results of chromium adsorption experiments of the adsorbents prepared at three different activation temperatures at different pH were tested (Fig. 1). Very clearly, biochar prepared at 400 °C had the best effect, and the removal rate was more than 98% at the pH of natural chromium solution (pH = 5.25), which was much milder than the acidic conditions reported in the literature. As shown in Table S2, Zp-pgBC-400 °C had the best removal effect, and the adsorption capacity reached 30.52 mg/g. And, the N\textsubscript{2} adsorption-desorption behavior of the Zp-pgBC-400 °C has been displayed in Fig. 2, which concluded that it had an excellent specific surface area (749.9 m\textsuperscript{2}/g) with a pore diameter of ~4.6 nm. It can be seen from Fig. 2, it had an obvious hysteresis loop, which belonged to the type IV adsorption curve and was an obvious adsorption curve of mesoporous adsorption materials. The nitrogen adsorption and desorption curves of materials calcined at 300 °C and 500 °C are shown in Fig. S1. The results showed that the specific surface area of the material calcined at 300 °C and 500 °C are 81.9 m/g and 1032.02 m\textsuperscript{2}/g, and the pore sizes are 10.41nm and 4.84 nm, respectively. The material calcined at 300 °C had the smallest specific surface area, least adsorption sites, which explained the poorest performance of Zp-pgBC-300 °C. Compared to 400 °C, the specific surface area increased at 500 °C, but the adsorption performance decreased. The decrease in the adsorption properties may be due to the decreases in the number of oxygen-containing groups at high temperatures (Calisto et al. 2014). The BET data were in good agreement with the experimental results (Fig. 1).
Fig. 1. Cr(VI) removal efficiency at three activation temperatures. (Initial concentrations = 50 mg/L, Solution pH 5.25, and T=25 °C).

Fig. 2. N\textsubscript{2} adsorption/desorption isotherms and pore size distribution curve of Z\textsubscript{PG}-BC-400 °C.

3.2 Cr(VI) adsorption studies

3.2.1 Effect of adsorbent dosage and pH

Adsorbent dosage and the pH of Cr(VI) solution are of particular importance in analyzing the adsorption procedure and exploring the adsorption ability (Suganya & Kumar 2018; Zhang et al. 2017). In Fig. 3(a), removal of Cr(VI) was studied at 25 °C and 160 rpm for 24 h in the initial concentration of 50 mg/L, with different dosage of
adsorbents. With the increase of adsorbent concentration in solution, the removal efficiency of Cr first increased rapidly, then reached a good removal efficiency (> 97.01%) at the adding = 1.5 g/L. Then with the increase of the amount of adsorbent, the adsorption capacity first tended to be stable and then decreased. Therefore, 1.5 g/L adsorbent can not only achieve a high removal rate but also achieve adsorption saturation.

The adsorption performance of biomass-based adsorbents may be closely related to the pH value of the solution, which affects both the existence of chromium and the charge properties of the adsorbent (Dong et al. 2011b; Yin et al. 2019; Zhang & Zheng 2015). As shown in Fig. 3(b), Cr(VI) had the maximum removal rate (> 97.01%) and higher adsorption capacity (31.4 mg/g) at pH ≤ 5.25. When the pH value is higher than 7, the removal rate and adsorption capacity decrease rapidly. At pH = 7, the removal efficiency of Cr(VI) was 78.2%, and only 55.92% when it increased to 9. With the increase of pH value, the removal rate was decreasing, which was because the pH value of the solution greatly affected the existence form of chromium species (Zhang & Zheng 2015).

Interestingly, the removal effect of chromium was not bad at a high pH value. Therefore, Fig. 3(c) measures the real-time change of pH value during the adsorption process. It can be observed that when the initial pH was 7.04 and 8.98, the pH of the solution decreased rapidly within 10 minutes after the adsorbent was added. After 200 minutes, the pH of all solutions hardly changed and reached equilibrium. The mechanism analysis showed that the rich oxygen-containing functional groups on the surface of biochar could keep the pH value of the solution at 3.1 - 5.41, when the initial pH value was 3.04 - 8.98. The species distribution of chromium species at different pH
values is shown in Fig. 3d. Combined with Fig. 3c, it is found that the main chromium species in the solution is HCrO$_4^-$, in which the removal mechanism can be explained by Eq. 3. This was a good explanation of why Z$_\text{p}$-pgBC-400 °C still had a good removal effect under alkaline conditions (See FTIR and XPS for more details).

$$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}^- \rightarrow \text{Cr}_3^+ + 4\text{H}_2\text{O} \quad (3)$$

**Fig. 3.** Effect of dosage (a) and solution pH (b) on Cr(VI) removal; (c)pH changing trend during reaction under various initial pH (5.25 was the intrinsic pH of the solution). T=298 K, C$_0$(VI)=50 mg/g, rpm=160

3.2.2 Adsorption kinetics
Various factors affecting Cr(VI) adsorption, and the contact time is one of the most important factors. Therefore, to study the adsorption kinetics, the time dependence of the Cr(VI) adsorption capacity on the Zr-pgBC had been investigated under optimum conditions. The four kinetics models were used to research the adsorption mechanisms: Pseudo-first order model (eq 4), Pseudo-second-order model (eq 5), Elovich model (eq 6), Intraparticle diffusion model (eq 7).

\[ q_t = q_e (1 - e^{-kt}) \]  \hspace{1cm} (4)

\[ q_t = \frac{k_2q_e^2t}{1+k_2q_e^t} \]  \hspace{1cm} (5)

\[ q_t = A + Blnt \]  \hspace{1cm} (6)

\[ q_t = k_it^{1/2} + C \]  \hspace{1cm} (7)

In Fig. 4(a), it was found that after 5 minutes, the removal amount of Cr(VI) reached 81.85%, and the adsorption capacity reached 26.84 mg/g, then gradually flat after 480 min. In Fig. 4(a) it can be known that the R-square value (R^2) of pseudo-second-order (R^2 = 0.999) was a little higher than that of the pseudo-first-order (R^2 = 0.946), which indicated that the rate-limiting step was a chemisorption process (Liang et al. 2020). Besides, the adsorption values calculated by the pseudo-second adsorption kinetic models (q2 = 32.05128 mg/g) were closed to the experimental data (32.458 mg/g). In Fig. 4(b), the results exhibited that the adsorption efficiency can be well fitted with the Elovich model with R^2 of = 0.9956, suggesting the existence of the chemical effect, and Cr(VI) adsorption was on the surface of heterogeneous solid adsorption (Guan et al. 2020). In Fig. 4(c), R^2 of the three-stage intraparticle diffusion model were greater than 0.99, indicating that the internal diffusion played a certain role in the actual adsorption process, but the lines have not been passed through the origin,
exhibiting that intragranular diffusion is not a speed limiting step.

Fig. 4. (a) Pseudo-first order and and Pesudo-second order; (b) Elovich model; (c) Intra-partice diffusion kinetic model; (d) Langmuir and Freundich adsorption isotherms; (e) Effects of original concentration on adsorption capacity at different temperature;(f)
Thermodynamic plot solution pH 5.25, mass of adsorbent=1.5 g/L, and T=25 °C).

3.2.3 Adsorption Isotherms

Two well-known adsorption isotherm models, Langmuir and Freundlich isotherm models, are commonly used to describe the adsorption process (Petkovska & Menka 2014). The equilibrium adsorption isotherms were investigated at three temperatures (25, 40, and 55 °C) with different initial concentrations of Cr(VI). The relevant parameters results were shown in Table S3 corresponding equations of Langmuir and Freundlich isotherms are represented as follows:

Langmuir model: \( q_e = \frac{KQc_e}{(1 + Kc_e)} \) (8)

Freundlich model: \( q_e = K_F c_e^n \) (9)

Where \( q_e \) (mg/g) is the equilibrium adsorption of Cr(VI) (mg/g), \( c_e \) (mg/L) is the equilibrium concentration in solution; \( q_{\text{max}} \) (mg/g) is the monolayer capacity of the adsorbent; \( K_L \) is the Langmuir constant related to the free energy of adsorption; \( K_F \) and \( n \) are the Freundlich constant and the heterogeneity factor, respectively.

In Fig. 4(d), It was obvious that the Langmuir model fitted the experimental data better. According to Table S3, the correlation coefficient (R^2), compared with the Freundlich model, the Langmuir model at three different temperatures showed a better fitting (R^2>0.95), which indicated that the adsorption process could be explained via the Langmuir model, can reflect that both physical and chemical adsorption are involved in the adsorption process and the maximum adsorption capacity was about 48.813 mg/g at 333 K. The results showed that the adsorption of Cr (VI) on the adsorbent was not caused by a single factor, but affected by a variety of adsorption processes.

3.2.4 Thermodynamic study
Thermodynamic study can reveal the feasibility and spontaneous nature of the adsorption process. Thermodynamic parameters are shown in Fig. S3. and Fig. 1. As shown in Fig. 4(e), with the increases in temperature, the adsorption capacity increased from 7.12 to 47.85 mg/g that higher temperature was beneficial to the adsorption process. When the initial concentration was more than 50 mg/L, the temperature has a significant effect on the removal of Cr(VI). To further explore the effect of temperature on adsorption efficiency, the thermodynamic parameters are determined using the following equations:

\[ \Delta G = -RT \ln k_c \]  
\[ \ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]  
\[ k_c = \frac{q_e}{c_e} \]

| T(K) | \( \ln k_c \) | \( \Delta G(\text{kJ/mol}) \) | \( \Delta H(\text{kJ/mol}) \) | \( \Delta S(\text{J/(mol.K)}) \) | \( R^2 \) |
|------|----------------|-------------------|-----------------|-----------------|--------|
| 298  | 2.835812       | -7.02593          | 73.27           | 269.2406        | 0.998  |
| 313  | 4.173052       | -10.339           |                 |                 |        |
| 328  | 5.543335       | -13.734           |                 |                 |        |

Where \( q_e \) and \( C_e \) are equilibration adsorption amount and equilibration adsorbate concentration, \( R \) (8.314 J /mol/k) is the universal gas constant, \( k_c \) is the distribution coefficient at each temperature (mg/L) and \( T \) is the absolute temperature. Enthalpy changes (\( \Delta H \)), entropy changes (\( \Delta S \)), free Gibbs energy (\( \Delta G \)) are three basic thermodynamics parameters associated with the adsorption process.

Thermodynamic constants and curves have shown in Fig. 4(e) and (f) and Table 1, respectively. When the initial concentration was greater than 50mg/L, the temperature
in increases significantly increased the adsorption capacity (Fig. 4(c)), and the linear fitted well between LnK₀ and 1/T (Fig. 4(f)) And usually, ΔH > 0 indicated that the reaction was an endothermic process. The positive ΔH value of 73.27 kJ/mol (Tabel 1) indicated the adsorption of Cr(VI) was an endothermic process (Chen et al. 2011). It should be noted that ΔH is generally in the range of 2.1-20.9 KJ/mol, which belongs to physical adsorption, while the chemical interaction involving complexation is usually between 20.9 - 418.4 KJ/mol (Rathinam et al. 2014). Therefore, the thermodynamic parameters well proved that the adsorption process in this study was a chemical adsorption process involving complexation. Besides, the positive ΔS > 0 (296.2406 J/mol/K) represented increasing in reaction system disorder, which was favorable to the adsorption reaction. And, ΔG < 0 manifested Cr(VI) adsorption on Zₚ-pgBC was a spontaneous reaction (Liu & Xu 2007). The ΔG values decreased when the temperature increased, which indicated that the spontaneous degree also increased with the temperature increasing.

3.2.5 Evaluation of selective adsorption

To investigate the selective properties of the Zₚ-pgBC-400 °C, adsorption of Cr(VI) in the presence of competitive ions in the binary system have been studied. Because Cr(VI) existed in the form of the anion in solution, only the influence of anion on its selective adsorption was studied. The concentration of Cr(VI) in all solutions was 50 mg/L. In Fig. 5, it can be seen that the removal efficiency of Cr(VI) was close to 100% (except CO₃²⁻) when the concentration of co-existing ions increases from 30 mg/L to 100 mg/L. To explore whether there was competitive adsorption between CO₃²⁻ and Cr, or whether the addition of CO₃²⁻ changed the inherent pH value of the solution, the pH value of the solution with CO₃²⁻ added was determined. The pH values
of 30, 50, 100 mg/L carbonate solution and the Cr ion coexistence solution were 6.26, 7.62, and 10.12, respectively. When the pH value of the solution added with carbonate was adjusted to about 5.20, the Cr(VI) removal rate was restored to nearly 100%. The reason was that the addition of carbonate changed the pH value of the solution, exceeding the pH window, resulting in a decrease in the adsorption effect. Therefore, the results indicated that the prepared $Z_{p} p g BC-400 \:^{\circ}C$ had high selectivity towards Cr(VI) in the presence of competitive ions, and it can recognize $Cr_{2}O_{7}^{2-}$ very well even in the presence of interfering ions to a quite high extent.

![Fig. 5. Effect of four common co-existing ions on Cr(VI) removal efficiency](image)

3.3 Characteristics and mechanism

3.3.1 XRD and FTIR analysis

Fig. 6(a) showed the XRD pattern of the adsorbed material. The strong broad peaks at 23° and 44° correspond to the crystal planes of (002) and (100) representing the typical graphitic carbon, which is often observed for pyrolyzed biomass carbons (Liu et al. 2014). Fig. 6(b) showed the infrared spectra before and after adsorption, on the whole, the positions of functional groups were almost unchanged before and after
adsorption, which may be the reason why the adsorbent can be removed efficiently after several times of adsorption and desorption. Functional groups in biochar are -OH (3000-3500 cm\(^{-1}\)), C=O/C=O-C (1680 cm\(^{-1}\)), -CH\(_2\) (2932, 2856 cm\(^{-1}\)), etc. The characteristic absorption bands at 2932 cm\(^{-1}\) and 2856 cm\(^{-1}\) belong to methylene stretching and bending vibrations (Chaofan et al. 2018). The characteristic peaks at 1680 and 1570 cm\(^{-1}\) were attributed to the stretching vibrations of C=C/C=O/C=O-C respectively due to generated polar functional groups on the Z\(_{p}p\)BC-400 °C after acid functionalization. And, the peak at 1134, 1057 cm\(^{-1}\) could be assigned to P-O/P=O groups (Chen et al. 2018). At peaks of 898 cm\(^{-1}\) and 804 cm\(^{-1}\), new substances were formed, which could be the vibration of Cr-O (Li et al. 2009). The FTIR results indicated that the adsorbent contained kinds of functional groups, such as -COOH, C=O, -OH, P=O/P-O, and R-C-O-C, which could provide numerous actives sites.

![Fig. 6](image.png)

**Fig. 6.** (a) XRD patterns, (b) FTIR spectra of Z\(_{p}p\)BC-400°C.

3.3.2 Structure and Morphology analysis

SEM is widely used to study the morphological and surface characteristics of the adsorbent materials. The surface morphological of raw materials (*Pennisetum giganteum*) and Z\(_{p}p\)BC-400 °C before and after adsorption are shown in Fig. 7. It can be observed that Fig. 7(a) presented a compact structure with low porosity and a
smooth surface. However, after mixed with phosphoric acid impregnation (Fig. 7(b) and Fig. 7(c)), the surface looked very rough with irregular cavities structure. This structural change may be due to the addition of phosphoric acid, a large number of irregular groups were introduced. From adsorption, this structure is conducive to adsorption. Moreover, for the difference between Fig. 7(c) and (b), which may be the result of the reaction between Cr and oxygen-containing functional groups on carbon materials. The rich distribution of C, O, and P elemental indicates the existence of a large number of oxygen-containing functional groups and Phosphorus oxygen functional groups on the Zp-pgBC-400 °C surface. Besides, the uniform distribution of chromium in Fig. 7(g) indicated that Cr(VI) was successfully adsorbed on the surface of Zp-pgBC-400 °C. The EDS mapping analysis results of Zp-pgBC-400 °C after adsorbing of Cr(VI) have been described in Fig. 7(d-g). Mapping results showed that that Cr(VI) contaminants have been homogeneously distributed. And the element content in Fig. 7(i). The prepared carbon materials have a large specific surface area (749.9 m²/g), large pore volume, rod-like porous structure, abundant P atoms, and abundant oxygen-containing functional groups.
Fig. 7 SEM images of *Pennisetum giganteum* (a); Z$_{\text{g}}$-pgBC-400 °C before (b) and after (c) Cr adsorption; Elemental mapping of (d) C, (e) O, (f) P, (g) Cr; (h) EDS point scan analysis area and (j) the corresponding EDS patterns.

3.3.3 XPS and morphology analysis

Besides element composition, XPS can also provide information on their valences of adsorbent and adsorbed species. The fine spectrum of C$_{1s}$ (Fig. 8 (a)) can be fitted to 3 peaks centered on the binding energies of about ~284.6 eV, ~286.0 eV, and ~289.4 eV, corresponding to the presence of C-C, C-O/C-P, and C=O bonds, respectively (Chen et al. 2018). The binding energy position and relative content of carbon changed little before and after use, indicating that the chemical state of the C element in biochar is relatively stable. Three peaks at about ~530 eV, ~532 eV, and ~534 eV in Fig.8(b) represented of C=O/P=O, C-O/P-O, and -OH/H$_2$O (Chen et al. 2020; Li et al. 2020). And, the O elements in the adsorption after also could observe three peaks. It is worth noting that the content of C-O/P-O (~532 eV) decreased, which indicated that the C-O/P-O bond was oxidized to C=O/P=O during the reaction (Xu et al. 2019a; Zhou et al. 2016b). And the binding energy of O shifted positively after the reaction, which indicated that the electron cloud density of O decreased, resulting in the detection of a higher binding energy band. In the process of Cr (VI) reduction, the O atom was the electron donor (Gao et al. 2013). This indicated that C-O/P-O participates in the adsorption and reduction of Cr(VI). Also, the fine spectrum of P$_{2p}$ has been changed
significantly. Attentively, for the phosphorus species, the strength of Z$_{p}$pgBC-400 °C decreased significantly after adsorption. And, the proportion of C-P decreased while C-P=O increased. The increase of C-P=O content indicated that after adsorption of Cr on biochar, the C-P bond of biochar was broken and the P=O bond was formed with chromate to form chromium phosphate. After adsorption, a new peak of CrPO$_4$ appeared at the binding energy of 133.4 eV (Fig. 8 (c)), which indicated that the P-containing group can interact and precipitate with some Cr (VI) ions. The fine spectra of Cr(VI) are shown in Fig. 8(d). Binding energies at 578.06 eV and 587.47 eV were assigned to Cr 2P$_{3/2}$ and 2P$_{1/2}$ orbitals of Cr(III), respectively (Xu et al. 2019b; Zhou et al. 2016a). The small peak at 582.21 eV was unreduced hexavalent chromium. Finally, in Fig. S2, the strength of C$_{1s}$/O$_{1s}$/P$_{2p}$ decreased after adsorption can be observed, and Cr$_{2p}$ appeared near 577 eV, further indicating that Cr was successfully adsorbed on the surface of biochar during the adsorption process.
3.3.4 Regeneration and adsorption/reduction mechanism

To investigate the reusability and stability of synthesized adsorbent, five times adsorption-desorption cycles were performed under the optimal conditions mentioned above. The details were as follows: before reusing, the used adsorbent should be filtered, then immersed in 0.1 M NaOH solution, stirred for 24 h, and then filtered and dried overnight in an oven at 80 °C. The results of five cycles were shown in Fig. 9. The removal efficiency of Cr(VI) decreased from 99.03% to 77.74% after cycles five times. After the fifth cycle, the Cr removal efficiency was more than 77%, which indicated that the synthesized adsorbent can be used many times without a significant decrease in adsorption capacity. This was much better than the stability after four uses reported by our research team (less than 70%) (Guan et al. 2020).

The results showed that Cr(VI) can be removed by the adsorption/reduction process in a wide range of operating pH. Based on the above analysis, the adsorption mechanism was proposed and systematically investigated (Fig. 10). There were many acidic groups on the surface of Zp-pgBC-400 °C, such as phosphate, carboxyl, carbonyl,
and so on. These acidic groups can release protons to maintain pH in a relatively narrow range when the external environment solution pH is relatively high. This can explain that the adsorbent can reach more than half of the removal rate under alkaline conditions. To sum up, the removal mechanism was shown in Fig. 10, including (1) electrostatic attraction; (2) physical adsorption in porous structures; (3) chemical reduction and adsorption, the most main adsorption process; and (5) metal complexation. The combined action of various functions is the reason why the adsorbent can effectively remove Cr(VI).

**Fig. 9.** Cycle times of Zₜ-pgBC-400 °C on Cr(VI) removal efficiency

**Fig. 10.** Schematic illustration of Cr(VI) removal mechanism

### 4. Conclusion

In this paper, biochar with enough acidic surface groups was synthesized, which
maintained the pH value of the system in a relatively stable range during the adsorption process. Cr(VI) uptake experiments displayed that in a wide pH range (1-6), the removal rate of Cr(VI) in water by biochar is as high as 86.39%. The mechanism analysis showed that the rich oxygen-containing functional groups on the surface of biochar could keep the pH value of the solution at 3.1-5.41 when the initial pH value was 3.04 - 8.98. The maximum adsorption capacity can reach 48.813 mg/g, and it is accorded with pseudo-second-order kinetics and L-type adsorption model. The results of five times adsorption-desorption experiments showed that the activated biochar directly impregnated with phosphoric acid had good stability. This work provided an effective solution for the removal of chromium in the pH range of a large window and opened up a new way for the resource utilization of *Pennisetum giganteum*, a common agricultural and forestry waste.

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Consent

Authors Contributions

Chenyao : Conceptualization, Validation, Formal analysis, Data curation, writing original draft. Ningping: Supervision, Project administration, Funding acquisition. Miaorongrong: Draft modification. Heliang: Investigation, Methodology, Writing-review & editing. Guanqingqing: Supervision, Project administration, Funding
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**Competing Interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Availability of data and materials**

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request. All data generated or analysed during this study are included in this published article [and its supplementary information files].

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Figure 1

Cr(VI) removal efficiency at three activation temperatures. (Initial concentrations = 50 mg/L, Solution pH 5.25, and T=25°C).
Figure 2

N2 adsorption/desorption isotherms and pore size distribution curve of Zp-pgBC-400°C.
Figure 3

Effect of dosage (a) and solution pH (b) on Cr(VI) removal; (c) pH changing trend during reaction under various initial pH (5.25 was the intrinsic pH of the solution). T=298 K, C0(VI)=50 mg/g, rpm=160
Figure 4

(a) Pseudo-first order and and Pesudo-second order; (b) Elovich model; (c) Intra-particle diffusion kinetic model; (d) Langmuir and Freundich adsorption isotherms; (e) Effects of original concentration on adsorption capacity at different temperature; (f) Thermodynamic plot solution pH 5.25, mass of adsorbent=1.5 g/L, and T=25°C).
Figure 5

Effect of four common co-existing ions on Cr(VI) removal efficiency

Figure 6

(a) XRD patterns, (b) FTIR spectra of Zp-pgBC-400°C.
Figure 7

SEM images of Pennisetum giganteum (a); Zp-pgBC-400°C before (b) and after (c) Cr adsorption; Elemental mapping of (d) C, (e) O, (f) P, (g) Cr; (h) EDS point scan analysis area and (j) the corresponding EDS patterns.
Figure 8

XPS spectrum of Zp-pgBC-400°C before and after Cr(VI) adsorption. (a) C1s, (b) O1s and (c) P2p and (d) Cr2p.
Figure 9
Cycle times of Zp-pgBC-400°C on Cr(VI) removal efficiency
Figure 10

Schematic illustration of Cr(VI) removal mechanism

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