Activated Carbon Developed from Amygdalus Pedunculata Shell for Cephalexin Removal: Kinetics and Equilibrium Study

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Abstract. Cephalexin (CEX) is widely used in aquaculture, animal husbandry, agriculture and forestry and other areas due to its wide antibacterial, high efficacy curative and less allergic reaction. However, exposure of antibiotics to the environment destroys the microecological balance and leads to an increase in bacterial resistance. Herein, low-price and high-efficiency activated carbon (AC) was produced from Amygdalus pedunculata shells (APS) by phosphoric acid and zinc chloride activation. The as-obtained AC shows high specific surface area of up to 1,810 m² g⁻¹ and 1,688 m² g⁻¹ prepared by ZnCl₂ and H₃PO₄ activation, respectively, and contains hierarchical structure of interconnected macro-, meso- and micropores. The maximum adsorption capacity for CEX based on the Langmuir model are 199.60 and 149.03 mg g⁻¹ by ZnCl₂ and H₃PO₄ methods, respectively. Therefore, the present AC produced from APS has potential as a low-cost adsorbent for CEX.

1. Introduction
As the first generation of cephalosporin, cephalexin (CEX) has the advantages of a wide antibacterial, high efficacy curative and less allergic reaction [1]. Therefore, it is widely in aquaculture, animal husbandry, agriculture and forestry and other areas [2]. Long-term exposure of antibiotics to the environment not only destroys the micro-ecological balance but also leads to an increase in bacterial resistance; this resistance ultimately induces the breeding of resistant bacterial strains, enables the formation of drug-resistant genes, and seriously threatens the safety of the entire ecosystem [3].

By convention, various techniques have been used to adsorption CEX, such as liquid membrane, nanofiltration, sonochemical degradation, enzymatic complexation, with minerals and functional polymers [4-9]. In recent years, adsorption has attracted the wide attention, for instance, mesoporous silica, metalorganic frameworks, and zeolites have been developed [10-14]. Among these, activated carbon adsorption has attracted the attention of many researchers due to its high specific surface area, developed pore structure and high adsorption efficiency [15].

Recently, various biomass carbons have been utilized as adsorption materials due to their low price, large storage capacity, eco-friendliness and renewable nature. Miao et al. studied alligator weed-activated carbon (AWAC), and the maximum CEX adsorption capacity was ~45 mg/g [16].
Ahmed et al. studied a human hair-derived high surface area porous carbon material (HHC), and the maximum CEX adsorption capacity of HHC was reported to be 210.18 mg/g at 50 °C [17].

Amygdalus pedunculata Pall (AP) is mainly available in arid, semiarid and desert areas in northwest China. It has outstanding capacity for soil conservation and sand fixation, displaying great potential in desert management, in the restoration of earth and rock slopes and in ecological forest construction [18]. Amygdalus pedunculata Pall seed shells (APS) account for 70% of the seeds and contain up to 48% carbon. Additionally, APS is regenerable, large storage capacity, cheap, and an eco-friendly biological waste precursor for preparing porous activated carbon (AC).

In this work, we prepare AC by using APS as the precursor material and zinc chloride (ZnCl₂) and phosphoric acid (H₃PO₄) as the activating agents. The pore structure was investigated. To study the adsorption properties of activated carbon, we evaluated the following parameters including initial CEX solution concentration, contact time, adsorbent dosage, temperature, and pH, on the adsorption properties of AC. Langmuir and Freundlich models were employed to determine which equations fit the experimental data [19]. For the kinetic data, pseudo-first order, pseudo-second order, and particle diffusion models were selected.

2. Experimental Section

2.1. Materials and Reagents
APS was collected from Shenmu County, Yulin City, Shanxi Province, China. CEX (λ=261 nm was purchased from Shanghai Yuanye Biological Technology Co., Ltd., China.

2.2. Characterization
The N₂ adsorption-desorption isotherms were obtained at 77 K using an ASAP2020 instrument. The specific surface area was calculated by the. Brunauer-Emmett-Teller (BET) method. Thermogravimetric analysis (TGA) was performed with a NETZSCH TG 209F 1 Iris 220-12-0055-L thermogravimetric analyser from 40 °C to 900 °C at a heating rate of 10 °C/min. UV-vis absorbance was measured at a wavelength of 261 nm using a UV-2102C spectrophotometer.

2.3. Preparation of AC
The dried APS was immersed in 50% ZnCl₂ solution with a ratio of 1.5 (ZnCl₂: APS, w/w) at room temperature (25±2 °C) for 24 h. The soaked and impregnated seeds were baked in an oven at 105 °C for 24 h and then placed in a muffle furnace. The materials are processed at 600 °C(10 °C/min) and the APS were kept at temperature for 120 min. As a comparison, APS was also soaked in 50% H₃PO₄ solution with a ratio of 2.0 (H₃PO₄: APS, w/w) at room temperature (25±2 °C) for 24 h and then placed in a muffle furnace. The temperature was raised to 400 °C at a heating rate of 10 °C min⁻¹ and the APS were kept at temperature for 120 min. The samples were washed with mixture solution of hydrochloric acid and deionized water with a ratio of 1:9 until the pH of was neutral, filtered and dried at 105 °C for 24 h.

2.4. Batch Adsorption Experiments
Batch equilibrium experiments were performed to study the effect of various operating parameters, such as pH, initial concentration and ionic strength, on CEX adsorption onto the two adsorbents. The adsorption experiments were performed on the mixture of 10 mg AC and 200 mL of CEX solution (15 mg L⁻¹). After a certain time, the supernatant liquid was filtered out.

The adsorption kinetic of the AC was calculated based on the following equation:

\[ q_e = \frac{(C_0 - C_e)V}{W_{AC}} \]  

where \( C_0 \) is the initial concentration of cephalixin solution, mg L⁻¹; \( C_e \) is the concentration of cephalxin in solution during adsorption equilibrium, mg L⁻¹; \( V \) is the volume of solution, L; and \( W_{AC} \)
is the mass of activated carbon, g.

2.5. Adsorption Kinetics
The adsorbed amount of CEX at a given time, \( q_t \) (mg g\(^{-1}\)), was determined by

\[
q_t = \frac{(C_0 - C_t)V}{W_{AC}}
\]

where \( C_t \) (mg L\(^{-1}\)) is the concentration of CFX solution at time t (min).

3. Results and Discussion

3.1. Characterization
The thermal stability of the APS was analysed by TGA (figure 1). The APS demonstrated an obvious weight loss from 260 to 390 °C. The APS had four thermal decomposition stages, which were observed at 40-260 °C, 260-300 °C, 300-390 °C and 390-600 °C. In the first phase, a weight loss of 3.9% was observed before 260 °C, which might be the loss of adsorbed water and small gas molecules from the APS. The weight of APS decreased sharply from 260 to 390 °C, which is due to the decomposition of cellulose and hemicellulose. The weight loss from 390-600 °C might be from the decomposition of lignin. The weight of APS was maintained at 22.3% after 600 °C, indicating that the AC prepared by APS can have a high yield of activated carbon.

Figure 2 shows powder X-ray diffraction (XRD) spectra over a wide angular range for the AC-H\(_3\)PO\(_4\) and AC-ZnCl\(_2\) materials. All the samples show diffraction peaks at 24.2° and 44°, corresponding to the (002) and (100) lattice planes of graphite, respectively, which indicates that the original structure was destroyed and converted into amorphous graphite crystallites during the preparation and activation of the carbon.

The \( N_2 \) sorption isotherm and pore size distribution of AC-H\(_3\)PO\(_4\) and AC-ZnCl\(_2\) are shown in figure 3. According to the IUPAC classification, the \( N_2 \) sorption isotherm curves of AC-H\(_3\)PO\(_4\) belong to the mixed model of types IV(a) and I(b), and AC-ZnCl\(_2\) belong to type I(b). When the relative pressure is low (\( P/P_0 < 0.1 \)), the nitrogen adsorption curves of the two ACs rise rapidly. The filling of micropores mainly occurs in this regime, indicating that both AC contain a certain number of microporous structures. When the relative pressure increases to \( P/P_0 \) of 0.1-0.3, the adsorption curve gradually deviates from the Y-axis and rises slowly, indicating that the two kinds of AC have a wide range of pore sizes, and both contain a mesoporous structure with a narrow pore diameter (less than 2.5 nm), which is type I(b); this type occurs when the relative pressure is low [20]. When the relative pressure continues to increase (\( P/P_0 > 0.4 \)), the adsorption amount of activated carbon to nitrogen is basically unchanged, and the adsorption stabilizes. According to the stable adsorption level and data in table 1, the pore volume of AC-H\(_3\)PO\(_4\) is slightly larger than that of AC-ZnCl\(_2\). When the relative pressure is large, the curve of AC-H\(_3\)PO\(_4\) gradually deviates and a hysteresis loop appears, indicating that the activated carbon is rich in mesopores. It was observed that AC-ZnCl\(_2\) does not have a hysteresis loop. According to the pore size distribution curves of the two activated carbons in figure 3b, AC-H\(_3\)PO\(_4\) has a pore size between 0 and 10 nm, and AC-ZnCl\(_2\) has a pore size between 0 and 4 nm. Table 1 show that the order of mesoporosity of the two AC is AC-H\(_3\)PO\(_4\) (81.1%) > AC-ZnCl\(_2\) (57%).

3.2. Adsorption of CEX

3.2.1. Effect of Contact Time. The adsorption amount increased quickly in the first hour which accounts for approximately 80% of the equilibrium adsorption amount (figure 4a). As the time extension, the adsorption amount slowed increased, and the adsorption reached an equilibrium level at 24 h. Therefore, the subsequent experiments were all conducted for 24 h because this was determined to be the adsorption equilibrium time. In addition, the order of the equilibrium adsorption amount of
the two activated carbons to cephalexin is AC-ZnCl₂ (150.58 mg g⁻¹) > AC-H₃PO₄ (117.32 mg g⁻¹).

![Figure 1. TG curves of the APS.](image)

![Figure 2. XRD spectrogram of activated carbon.](image)

![Figure 3. (a) N₂ adsorption-desorption isotherms of AC-H₃PO₄ and the AC-ZnCl₂ and (b) pore size distribution of AC-H₃PO₄ and the AC-ZnCl₂.](image)

**Table 1.** BET surface area and pore structure parameters of activated carbons.

| Sample       | S_BET (m²·g⁻¹) | V_tot (cm³·g⁻¹) | V_mes (cm³·g⁻¹) | V_micro (cm³·g⁻¹) | D_av (nm) |
|--------------|----------------|-----------------|-----------------|-------------------|-----------|
| AC-ZnCl₂     | 1810           | 0.931           | 0.531           | 0.102             | 2.15      |
| AC-H₃PO₄     | 1688           | 1.021           | 0.828           | 0.017             | 2.44      |

3.2.2. Effect of Solution pH. The pH was the range of 2-9. Figure 4b shows the plots of CEX removal percentage and equilibrium adsorption quantity. For AC-ZnCl₂, when the initial pH value was between 3 and 7, the adsorption amount maintains a large stable value, and when the initial pH value was less than 3 or greater than 7, the adsorption amount decreased. The optimum solution has an initial pH of 7. For AC-H₃PO₄, the initial pH of the solution was between 3 and 6, and the amount of CEX also increased and reached a maximum; however, adsorption steadily declined after pH of 3.

3.2.3. Effect of Temperature. A temperature change will impact the dissociation equilibrium of CEX and the viscosity of the solution, which will affect the adsorption. As the adsorption temperature increased, the adsorption capacity of activated carbon for CEX increased to different extents, as shown in figure 4c. There may be two possible reasons for these results: (1) A temperature increase causes the dissociation balance of CEX change. This change is beneficial to its adsorption on the surface. (2) A temperature increase lowers the viscosity of the solution, makes CEX more soluble in the solution, and increases the contact between the AC and CEX, promoting adsorption.
3.2.4. Effect of Solution Ionic Strength. The adsorption of CEX by AC-ZnCl$_2$ and AC-H$_3$PO$_4$ is not sensitive to ionic strength, probably because CEX forms an inner surface complex with these two ACs, which are covalently bonded (figure 4d). The concentration of NaCl in the solution was maintained at 0.002 mol L$^{-1}$ in the subsequent adsorption experiments.

3.2.5. Adsorption Kinetics. Adsorption kinetics are an important means of analysing and describing the adsorption process. To study the adsorption process of activated carbon on cephalexin, the kinetics data were analysed by a pseudo-first-order model, pseudo-second-order model, and intraparticle diffusion model [21]. The mathematical forms of these models show below.

Pseudo-first order dynamics model:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Pseudo-second order dynamics model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $q_t$ and $q_e$ correspond to the adsorption amount of activated carbon to CEX at time and at the adsorption equilibrium, respectively, mg g$^{-1}$; $k_1$ is the pseudo-first order adsorption rate constant, h$^{-1}$; and $k_2$ is the pseudo-second-order adsorption rate constant, g (mg·h)$^{-1}$.

The experimental data in figure 5 and table 2 have a better fit with the pseudo-second order kinetic equation, where the correlation coefficient is greater than 0.99, and the equilibrium adsorption amount calculated from the fitting equation is more than the experimental value. This indicates that the pseudo-second-order model can accurately reflect the adsorption process of AC-H$_3$PO$_4$ and AC-ZnCl$_2$ on CEX and that each adsorption process is controlled by chemical adsorption.
Figure 5. The kinetics models for adsorption of CEX on the AC-H₃PO₄ and AC-ZnCl₂: (a) pseudo-first order model; (b) pseudo-second order model.

Table 2. Kinetic parameters for adsorption of CEX on activated carbon.

| Adsorbate    | C₀ (mg/g) | Pseudo-first-order | Pseudo-second-order |
|--------------|-----------|--------------------|---------------------|
|              |           | K₁ (h⁻¹)          | qₑ (exp)            | R²                  | K₂ (g·(mg·h)⁻¹) | qₑ (exp) | R²       |
| AC-ZnCl₂     | 150.58    | 0.1729             | 45.62               | 0.8789             | 0.0256           | 150.38    | 0.9988   |
| AC-H₃PO₄     | 117.32    | 0.1726             | 35.91               | 0.8790             | 0.0450           | 116.82    | 0.9995   |

Combined with the data in figure 6, table 3 shows that the adsorption isotherm for cephalexin adsorbed on the two activated carbons is more consistent with the Langmuir model, where the correlation coefficient is higher than 0.99. According to the basic hypothesis of the Langmuir model, cephalexin can be inferred. The adsorption on the surface of each AC tends to be homogeneously adsorbed by a single layer. This may due to the uniform distribution of pores, functional groups and active sites on the surface of the activated carbon, which results in the same adsorption activation energy for each cephalexin molecule. According to the Langmuir fitting curve, the maximum adsorption capacity of each AC to CEX at room temperature is: AC-ZnCl₂ (199.60 mg⁻¹) > AC-H₃PO₄ (149.03 mg⁻¹).

Figure 6. The adsorption isotherm models for adsorption of CEX on the AC-H₃PO₄ and AC-ZnCl₂: (a) Langmuir model and (b) Freundlich model.
Table 3. Adsorption parameters of Langmuir and Freundlich equation.

| Sample       | Langmuir model | Freundlich model |
|--------------|----------------|------------------|
|              | $q_m$ (mg·g$^{-1}$) | $K_L$ (L·mg$^{-1}$) | $R^2$ | $K_F$ | $n$ | $R^2$ |
| AC-ZnCl$_2$  | 199.60          | 0.59             | 0.9981 | 82.84 | 3.02 | 0.9516 |
| AC-H$_3$PO$_4$ | 149.03         | 0.95             | 0.9983 | 85.27 | 4.96 | 0.9710 |

4. Conclusions
Activated carbons possessed high mesopore contents were prepared by ZnCl$_2$ and H$_3$PO$_4$ activation agricultural waste, namely, APS were used as precursors for the preparation of both carbons. In this work, the equilibrium adsorption data of CEX fits the Langmuir isothermal model and the adsorption capacities of AC-ZnCl$_2$ and AC-H$_3$PO$_4$ are 199.60 and 149.03 mg·g$^{-1}$. The adsorption kinetic data agree well with the pseudo-second-order model. According to the data, we can conclude that the H$_3$PO$_4$ activated AC shows the best adsorption of CEX. This work provides a green, cost-effective and environmentally friendly strategy for the preparation of porous AC materials that can be used for the removal of CEX from aqueous solutions.

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