Adsorption of ampicillin sodium on activated carbons with different surface chemistries

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Abstract. BACKGROUND: The adsorption of ampicillin from aqueous solution by three types of activated carbon was investigated. The first was a commercial activated carbon (AC), the second (AAC) was AC modified by HNO3 oxidation and the third (HAAC) was AAC modified through thermal treatment. The surface properties of the activated carbon samples were characterized and the effects of pH and contact time on the adsorption were determined. The adsorption isotherms, adsorption kinetics and adsorption mechanism are discussed.

RESULTS: Compared to AC, HNO3 oxidation increased the number of acid functional groups on the surface of AAC, which hindered the adsorption of ampicillin. For HAAC, thermal treatment removed surface oxygen groups and then improved the adsorption ability. The adsorption processes was greatly affected by pH and acidic conditions were favorable for adsorption. With an initial ampicillin sodium concentration of 200 mg/L, 9 h was needed for adsorption to reach equilibrium. The Langmuir isotherm provides a better fit for the adsorption than the Freundlich isotherm and the maximum adsorption capacities for AC, AAC and HAAC were 90.6, 59.8, 140.9 mg/g, respectively. The sorption kinetics can be described by a pseudo-second order model. CONCLUSION: The functional groups on activated carbon greatly affect its adsorption ability. The adsorption of ampicillin can be improved by increasing the number of basic functional groups on the activated carbon. Chemisorption was the dominant adsorption process and pH was an important factor affecting ampicillin adsorption.

1. Introduction
Pharmaceutical compounds are an important source of water pollutants because of their large variety and high consumption rates, as well as their persistence in the environment. Their presence may cause potential health effects in humans and may also affect aquatic organisms. Many pharmaceutical compounds have been detected in water and have been recognized as some of the hazardous chemical substances able to affect the natural equilibrium system of the surrounding environment [1-4].

Among all the pharmaceutical drugs that cause contamination of the environment, antibiotics occupy an important place due to their high consumption in both veterinary and human medicine. There are many reports on the occurrence of antibiotics in the aquatic environment [5-10]. Exposures to low-level antibiotics in the environment have raised significant concern [11].

Ampicillin is a β-lactam that has been used extensively to treat infections caused by both gram-positive and gram-negative bacteria. Ampicillin and other ampicillin-like β-lactams, are some of the most important antibiotics used worldwide, for both humans and animals. Currently, ampicillin is used...
to treat a wide range of diseases and infections. It is also known to be resistant to degradation, remaining as an active compound in urine and human feces [12]. The existence of ampicillin in the environment causes some potential problems due to an increase of ampicillin-resistant bacteria. It is thus of great importance to develop efficient and cost-effective treatment technologies for removal of such compounds.

Adsorption techniques using solid adsorbents are widely used to remove various organics from wastewater. Among all the adsorbent materials proposed, activated carbon is the most popular for the removal of pollutants from aqueous solution. Granular Activated Carbon (GAC) with high porosity offers a large specific surface area for adsorption, and has been widely used to remove organic contaminants from water and wastewater. This method is simple, has low operation costs in comparison to other techniques, and is applicable to treatment of many common substances [13-14].

The adsorption capacity of GAC is determined not only by the textural properties but also by the chemical nature of its surface, i.e., the amount and nature of oxygen-containing functional groups [15-16]. There are already many reports on the role of the GAC surface chemistry in the adsorption of organic contaminants from wastewater, such as dyes, humic substances and phenolic compounds [17-20]. However, little attention has been given to the role of the GAC surface chemistry in the adsorption of drugs, especially antibiotics.

The main objective of this work is to present and discuss the characteristics and adsorption properties of activated carbons with different surface chemistries in the removal of ampicillin. HNO3 was used to create more acid functional groups, while subsequent thermal treatment was used to produce basic functional groups. The influence of the functional groups and other parameters (i.e., surface area, contact time, pH) on the sorption capacity of these carbons were evaluated.

2. Experimental

2.1. Chemicals and reagents
Ampicillin sodium (C16H18N3NaO4S) was purchased from Bio Basic (USP grade, Canada). GAC (analytical grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. The GAC was sieved between 20 and 40 mesh size. The material had a BET surface area of 967.71 m²/g. Folin-Ciocalteu phenol reagent was purchased from Sangon Biotech (Shanghai).

2.2. Preparation activated carbon samples
Prior to use, the original carbon was washed with boiled deionized water for 3 h and oven-dried at 110 °C for 24 h (AC).

2.3. Chemical treatment using nitric acid
Nitric acid oxidation was carried out as follows: AC (5.0 g) was added to a concentrated HNO3 solution (4 mol/L, 100 mL) in a flask. The solution was then stirred with a magnetic stirrer for 24 h at room temperature. Then the material was filtered, extensively washed with distilled water until neutral pH, and then dried at 110 °C for 24 h. The sample was referred to as AAC.

2.4. Thermal treatment
Thermal treatment was performed on AAC, since it is important that the starting material presents more surface groups and this would be helpful to produce activated carbons with a higher basicity [21]. About 3.0 g of AAC was placed in a fused silica tubular reactor, heated to 800 °C at 10 °C/min under a flow of N2 (50 cm³/min) and kept at this temperature for 3 h. After cooling to room temperature under the same atmosphere, a flow of air was introduced into the reactor and these conditions were maintained for 1 h. Then the sample (HAAC) was collected and stored in a dessicator.
2.5. Characterisation of activated carbon samples

The BET surface area ($S_{BET}$), total pore volume and pore size distribution (PSD) of the samples were obtained from N$_2$ adsorption-desorption isotherms at 77 K using an automatic adsorption apparatus (JW-BK122W, Beijing JWGB Sci & Tech Co., Ltd.). The BET surface area $S_{BET}$, the total pore volume ($V_{tot}$) and the pore width ($D_w$) were provided by the manufacturer's software. The t-plot method was used to calculate the micropore surface area ($S_{mic}$) and the micropore volume ($V_{mic}$). The external volume ($V_{ext}$) and the external area ($S_{ext}$) were calculated by subtracting $V_{mic}$ from $V_{tot}$ and $S_{mic}$ from $S_{BET}$, respectively.

The acidic surface functional groups on samples were determined using Boehm's titration method[22]. The Boehm method is described as follows: 0.5 g of carbon was added to a series of flasks containing 50 mL of 0.05 mol/L NaOH, Na$_2$CO$_3$, NaHCO$_3$, and HCl solutions. The flasks were then sealed and shaken for 24 h at room temperature. The suspensions were then decanted and 10 mL of the remaining solution was titrated with 0.05 mol/L HCl or NaOH, depending on the original solution used. The number of acidic groups was calculated based on the assumptions that NaOH neutralizes carboxylic, lactonic, and phenolic groups; Na$_2$CO$_3$ neutralizes carboxylic and lactonic groups; and NaHCO$_3$ neutralizes only carboxylic groups. The number of basic sites was determined from the amount of HCl that reacted with the carbon.

The determination of the pHpzc of the samples was carried out as follows: 50 mL of 0.01 mol/L NaCl solution was placed in a closed Erlenmeyer flask. The pH was adjusted to a value between 2.0 and 10.0 by adding HCl (0.1 mol/L) or NaOH (0.1 mol/L) solutions. Then, 0.15 g of each GAC sample was added and the final pH measured after 48 h under agitation at room temperature. The pHpzc is the point where the curve of pH$_{final}$ vs. pH$_{initial}$ crosses the line pH$_{initial}$=pH$_{final}$.

2.6. Adsorption of ampicillin on the activated carbons

The adsorption of ampicillin sodium was carried out as follows. In each adsorption experiment, 100 mL of ampicillin sodium solution of known concentration was added to a 250-mL round bottom flask at 30 °C. NaOH (0.1 mol/L) and H$_2$SO$_4$ (0.1 mol/L) were used to adjust the initial pH of the solution. The flasks were kept in a thermostatted shaker bath and agitated at 150 rpm/min to reach equilibrium.

The kinetics of sorption were determined by analyzing the adsorptive uptake of ampicillin sodium from aqueous solutions at different time intervals to determine when adsorption equilibrium was reached and the maximum removal of the pollutant was attained. The carbon was removed before measurements and the samples were filtered through a 0.45 µm membrane syringe filter to measure the residual ampicillin sodium concentration. The method for the determination of ampicillin sodium concentration was according to Ahmad. The amount of ampicillin sodium adsorbed onto activated carbon was calculated using the following expression:

$$q_e = (C_0 - C_e)V/m$$  \hspace{1cm} (1)

where $q_e$ is the equilibrium adsorption capacity of ampicillin sodium adsorbed per unit mass of activated carbon (mg/g); $C_0$ and $C_e$ are the initial ampicillin sodium concentration (mg/L) and ampicillin sodium concentration (mg/L) at equilibrium, respectively; V is the volume of the ampicillin sodium solution (L); and m is the weight of activated carbon (g).

3. Results and discussion

3.1. Characterisation of activated carbon samples

The parameters of textural characteristics of samples are shown in Table 1. It can be seen that the $S_{BET}$ and $V_{micro}$ of AAC and HAAC lowered after modification. For AAC, the $S_{BET}$ decreased about 10%. In the oxidation process, HNO$_3$ destroyed pore walls, leading to decreases of surface area and pore volume. The pore entrances can also be blocked by the introduction of oxygen functional groups which also reduce the $S_{BET}$. 
After thermal treatment, there was a slight increase of $S_{BET}$ for HAAC. It is possible that some oxygen functional groups were not stable at high temperatures, so their removal increased $S_{BET}$, similar to the results obtained in Chingombe's work.

The activated carbon was predominantly microporous. The percentage of micropore area for the samples was between 85.3% and 86.3%. The change of $V_{micro}$ showed a similar trend as $S_{BET}$. The average pore diameters did not show significant differences and the pore diameters of the three samples were all about 2.1 nm, indicative of their microporous character.

The adsorption isotherms of nitrogen on AC, AAC, and HAAC are shown in Figure 1. The $N_2$ adsorption isotherms were classified as type I, characteristic of microporous solids, according to the IUPAC classification. It also can be seen that the adsorption capacity of $N_2$ corresponds to the value of $S_{BET}$.

The acidity and basicity of the samples and the values of pHpzc are shown in Table 2. Surface functional groups such as carboxyl, lactone, phenol or carboxylic anhydride are likely the source of surface acidity. It can be seen from the table that the pHpzc of AC was 4.4 and there were few functional groups on the activated carbon. After oxidation (AAC), the number of acidic functional groups increased and pHpzc decreased to about 3.0. After AAC was subjected to thermal treatment, acidic functional groups were removed and the basicity increased. For AAC and HAAC, the number of functional groups was still low, which may due to the limited number of functional groups on the original carbon and the mild oxidation conditions.

| Sample | $S_{BET}$ (m$^2$/g) | Micropore area (m$^2$/g) (%) | Average pore diameter (nm) | $V_{micro}$ (cm$^3$/g) |
|--------|----------------------|-----------------------------|--------------------------|------------------------|
| AC     | 967.71               | 835.08 86.3                 | 2.13                     | 0.356                  |
| AAC    | 891.51               | 763.23 85.6                 | 2.16                     | 0.329                  |
| HAAC   | 912.76               | 778.67 85.3                 | 2.17                     | 0.334                  |

**Figure 1.** $N_2$ adsorption-desorption isotherms of GACs.

**Table 2.** Surface chemical characteristics of the GAC samples.

| Sample | Carboxylic (mmol/g) | Lactonic (mmol/g) | Phenolic (mmol/g) | Acidity (mmol/g) | Basicity (mmol/g) | pHpzc |
|--------|---------------------|-------------------|-------------------|-----------------|-------------------|-------|
| AC     | 0.030               | 0.017             | 0.062             | 0.129           | 0.067             | 4.4   |
| AAC    | 0.097               | 0.045             | 0.105             | 0.247           | 0.011             | 3.0   |
| HAAC   | 0.012               | 0.00              | 0.00              | 0.012           | 0.144             | 7.2   |
3.2. Effect of pH

The pH is an important factor affecting the adsorption behaviour. The pH of the solution strongly affects the structure of the ampicillin antibiotic. At pHs between 2.9 and 7.2, it shows a zwitterionic structure; but at pHs above 7.2, an anionic structure is the predominant species, as shown in Figure 2.

In this experiment, the effects of pH on the removal of ampicillin were determined over a pH range of 3.0-9.0. In the experiment, 0.3 g of activated carbon was added to 100 mL of ampicillin sodium solution (200 mg/L) and adsorbed for 2 h, then the concentration of antibiotic in the solution was tested.

The effect of pH is shown in Figure 3. The maximum removal efficiency can be achieved at pH 4.0 for AC and pH 3.0 was favorable for the adsorption of modified activated carbons (AAC and HAAC). The removal efficiency decreased with the increase of pH for all three samples.

The pHpzc of AC and AAC were 4.4 and 3.0, respectively. At pH around pHpzc, the two activated carbons gave the highest removal performance. At pH around 4.0, the electrostatic force would enhance the adsorption capacity for AC. Under this condition, the positively and negatively charged functional groups on ampicillin would be attracted by the negatively and positively charged functional groups on AC.

At pH 3.0, ampicillin was mainly positively charged. When pH>3.0 (pHpzc of AAC), -COOH would ionize to -COO- and AAC would be negatively charged, then the repulsive force between adsorbent and adsorbate would increase and lead to a reduction of adsorption.

But for HAAC, the situation was different, the best removal performance was achieved at pH 3.0, not pH 7.2. The reason may due to the chemical-sorption mechanism. H+ adsorbed on activated carbon and integrated with -NH₂ may also participate in chemical reactions, resulting in a higher adsorption on activated carbon. In Putra and Pranowo's work on amoxicillin, they also proposed that more functional groups were protonated at low pH, in comparison to that at high pH, and then more interaction between amoxicillin and activated carbon could be expected. As the structure of amoxicillin is very similar to ampicillin, the adsorption on activated carbon may be similar from the view of the chemical-sorption mechanism.

In the adsorption process of ampicillin, both of these mechanisms may co-exist and the latter plays an important role, especially for HAAC.

Figure 2. Effect of pH on the charge of ampicillin.

Figure 3. Effect of pH on ampicillin removal efficiency.
3.3. Effect of contact time

A plot of removal efficiency versus contact time is shown in Figure 4. The initial concentration of ampicillin sodium solutions was 200 mg/L and the pHs of AC, AAC and HAAC were adjusted to 4.0, 3.0 and 3.0, respectively. Within the initial 4 h, the amount of ampicillin sodium adsorbed increased quickly. Then the removal efficiency increased slowly and 9 h was needed for adsorption to reach equilibrium for all three samples. In the adsorption isotherm experiments, the equilibrium time was set to 10 h.

3.4. Adsorption isotherms

The equilibrium isotherm data for adsorption of amoxicillin onto activated carbons were fit with the Langmuir and Freundlich models. The results were analysed using Langmuir and Freundlich isotherms:

\[ q_e = q_m K_L C_e / (1 + K_L C_e) \]  

and

\[ q_e = K_F C_e^{1/n} \]

respectively, where \( C_e \) and \( q_e \) are the adsorbate equilibrium concentrations in the liquid and solid phases, \( q_m \) is the maximum adsorption capacity in the Langmuir model, \( K_L, K_F \) and \( n \) are constants.

The adsorption isotherms and parameters are presented in Figure 5 and Table 3. It can be seen the Langmuir adsorption isotherm provides the best fit for the adsorption of ampicillin on the three activated carbons. The calculated values of \( q_m \) for AC, AAC and HAAC were 90.6, 59.8, 140.9 mg/g, respectively. The adsorption ability of AAC was greatly decreased after HNO3 oxidation and the percentage decreased about 23% compared to AC. Though the \( S_{BET} \) of HAAC was smaller than AC, its adsorption of ampicillin was 50% higher than that of AC. Therefore the decrease of \( S_{BET} \) was not the only factor affecting the adsorption process.

The values of \( n \) in the Freundlich isotherms were all above 1 and this meant ampicillin can be easily adsorbed on activated carbons. It also can be seen that the values of \( n \) correspond to the adsorption capacities.

| Sample | \( K_L \)  | \( q_m \) (mg/g) | \( R^2 \) | \( K_F \)  | \( n \) | \( R^2 \) |
|--------|----------|-----------------|---------|----------|-------|---------|
| HAAC   | 0.0224   | 140.85          | 0.9929  | 18.80    | 2.96  | 0.9736  |
| AC     | 0.0110   | 90.57           | 0.9943  | 5.858    | 2.30  | 0.9796  |
| AAC    | 0.00997  | 59.84           | 0.9908  | 3.280    | 2.22  | 0.9915  |
3.5. Adsorption kinetics
The kinetics for adsorption of amoxicillin onto bentonite and activated carbon were also examined. The pseudo-first, second order and Elovich models were employed to correlate the kinetics data.

3.6. The pseudo first-order equation
The pseudo first-order equation is expressed as:
\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

After integration and applying boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_e\), the integrated form of Eq. (4) becomes:
\[
\ln(q_e - q_t) = \ln(q_e) - k_1t
\]

where \(q_t\) and \(q_e\) are the amounts of amoxicillin adsorbed at time \(t\) and equilibrium (mg/g), respectively, and \(k_1\) is the pseudo first-order rate constant for the adsorption process (1/min).

3.7. The pseudo-second order model
The sorption kinetics may be described by a pseudo-second order model. The differential equation is the following:
\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

where \(q_e\) is the amount of amoxicillin adsorbed at equilibrium (mg/g), \(q_t\) is the amount of amoxicillin adsorbed at time \(t\) (mg/g) and \(k\) is the equilibrium rate constant of pseudo-second order sorption (g/(mg min)). Integrating Eq. (6) for the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t = q_e\) gives:
\[
\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t
\]

which is the integrated rate law for a pseudo-second order reaction. Eq. (7) can be rearranged to obtain a linear form:
\[
t/q_t = \frac{1/k_2}{q_e} + t/q_e
\]

and \(h = kq_e\), where \(h\) is the initial sorption rate (mg/(g min)).

The rate parameters \(k\) and \(q_e\) can be directly obtained from the intercept and slope of the plot of \(t/q_t\) against \(t\) (Figure 6(b)). Values of \(k\) and \(q_e\) are listed in Table 4. It was clear that the kinetics of adsorption on carbon materials follow the second-order model as the plots of \(t/q_t\) versus \(t\) give a linear relationship. The calculated \(q_e\) values agree with the experimental \(q_e\) values, and also the regression coefficients were above 0.99. These results suggest that the pseudo-second order mechanism is predominant which means that chemisorption might be the rate-limiting step that controls the adsorption process.
3.8. The Elovich equation

The adsorption data may also be analyzed using the Elovich equation, which has the form:

\[
\frac{dq_t}{dt} = \alpha e^{-\beta t}
\]

(9)

where \(\alpha\) is the initial adsorption rate constant (mg/(g·min)) and the parameter \(\beta\) is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich equation can be simplified by assuming that \(\alpha \beta t \ll 1\) and the integration of the rate equation with the same boundary conditions as the pseudo first-and second-order equations becomes the Elovich equation:

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

(10)

**Figure 6.** (a) First-order kinetics model. **Figure 6.** (b) Pseudo-second-order kinetics model. **Figure 6.** (c) Elovich equation model.

| Samples | \(q_e\) | \(k_1\times10^{-3}\) | \(R^2\) | \(q_e\) | \(k_2\times10^{-4}\) | \(R^2\) | \(\alpha\) | \(\beta\) | \(R^2\) |
|---------|--------|-----------------|--------|--------|-----------------|--------|--------|--------|--------|
| AC      | 47.7   | -7.0            | 0.9157 | 52.44  | 2.685           | 0.9969 | 2.62×10^{-3} | 10.04  | 0.9937 |
| AAC     | 30.6   | -6.3            | 0.9581 | 33.56  | 4.036           | 0.9932 | 5.75×10^{-3} | 6.16   | 0.9815 |
| HAAC    | 59.6   | -8.1            | 0.9602 | 64.60  | 2.928           | 0.9984 | 9.56×10^{-3} | 11.34  | 0.9927 |

**Table 4.** Kinetic parameters and correlation coefficients \((R^2)\) for different kinetic models.

It can be seen from Figure 6 and Table 4 that the pseudo-second order model correlates with the kinetic data much better \((R^2 > 0.99)\) than the first-order kinetics model and the Elovich equation model. The plot of \(v/q_e\) versus \(t\) (Figure 3) yields very good straight lines for different samples. We therefore conclude that chemisorption plays an important role in the adsorption.
The values of parameters $q_e$ and $k$ ($k_1$ for pseudo-first order and $k_2$ for pseudo-second order) suggest different adsorption abilities of the activated carbon samples.

3.9. Adsorption mechanism
The modification of activated carbon changed the $S_{BET}$ and surface chemistry of activated carbons in the experiment. Both of the factors affected the adsorption process. Compared to AC, the $S_{BET}$ of AAC was reduced after HNO$_3$ oxidation, which led to a decrease of adsorption ability. However, the ability was elevated for HAAC. Therefore $S_{BET}$ is not necessarily proportional to the adsorption capacity and the adsorption is greatly affected by surface functional groups.

The oxidation process produced more surface oxygen groups and altered the hydrophilicity and polarity of AAC. The sample became more hydrophilic and then more water was adsorbed, which would form clusters that block the dispersion of ampicillin molecules to the adsorption sites. Also, functional groups which are electron-withdrawing, can reduce the adsorptive ability by attracting the free π electrons from the basal planes of the activated carbon. The effect would decrease the π electron density and then led to the weakness of the interactions between the π electrons of the AAC and aromatic ring on the ampicillin molecule. At the same time, the electrostatic interactions may also affect the adsorption process, especially for AC and AAC. Oxygen functionalities were removed for HAAC, making the carbon surface less polar, which strengthened the affinity for ampicillin adsorption.

4. Conclusions
The functional groups on activated carbons greatly affect the adsorption process of ampicillin from water. Acid groups on HNO$_3$-treated carbon impaired the adsorption process, while their absence after thermal treatment favored the adsorption of ampicillin. The pH greatly affected the behavior of adsorption, and acidic conditions (pH 3.0-4.0) favored the adsorption process for all the activated carbons.

The equilibrium isotherm data for adsorption of ampicillin onto activated carbons were also modeled using the Langmuir and Freundlich models. Langmuir isotherms provide the better fit for the adsorption. The maximum adsorption capacities for AC, AAC and HAAC are 90.6, 59.8, 140.9 mg/g, respectively.

The kinetic data were fitted to a pseudo-first-order kinetic model, pseudo-second-order kinetic model and the Elovich equation model. The pseudo-second-order kinetic model best fit the data which indicated that chemisorption is dominant and controls the adsorption.

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