Sorption of tetracycline on biochar derived from rice straw under different temperatures

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Abstract

Biochars produced from the pyrolysis of waste biomass under limited oxygen conditions could serve as adsorbents in environmental remediation processes. Biochar samples derived from rice straw that were pyrolyzed at 300 (R300), 500 (R500) and 700˚C (R700) were used as adsorbents to remove tetracycline from an aqueous solution. Both the Langmuir and Freundlich models fitted the adsorption data well (R² > 0.919). The adsorption capacity increased with pyrolysis temperature. The R500 and R700 samples exhibited relatively high removal efficiencies across a range of initial tetracycline concentrations (0.5mg/L-32mg/L) with the maximum (92.8%–96.7%) found for adsorption on R700 at 35˚C. The relatively high surface area of the R700 sample and π–π electron-donor acceptor contributed to the high adsorption capacities. A thermodynamic analysis indicated that the tetracycline adsorption process was spontaneous and endothermic. The pH of solution was also found to influence the adsorption processes; the maximum adsorption capacity occurred at a pH of 5.5. These experimental results highlight that biochar derived from rice straw is a promising candidate for low-cost removal of tetracycline from water.

Introduction

Antibiotics are widely used to control infectious diseases and as animal feed additives to promote healthy growth. In China in 2013, annual antibiotics consumption was approximately 162,000 tons, with 52% of the total attributed to animal use [1]. Such levels of consumption notably increase the environmental concentration of antibiotics. This is because animals only absorb a portion of the dosage given to them and a large volume of antibiotics is then excreted via urine and feces [2]. These residual antibiotics can then be taken up from the environment by plants and animals, and can even accumulate in the human food chain [3, 4]. In addition, the persistent levels of antibiotics in the environment promotes antibiotic resistance via gene transfer within, particularly pathogenic, bacteria [5]. Tetracycline is one of the most extensively used antibiotics and is often used in the livestock industry where wastewater analysis has shown tetracycline concentrations reaching tens of micrograms per liter [1, 6].
There are a number of methods available to combat antibiotic contamination of wastewater and the wider environment. These can generally be categorized as processes that employ advanced oxidation, electrochemistry, a biological agent, or a sorption system [7–9]. Adsorption is one of the most efficient means of limiting antibiotic contamination and displays advantages such as low cost, simple design and easy operation [10]. Adsorption processes have been used to remove around 30 types of antibiotics with removal efficiencies in the 90–100% range at mg/L concentration levels in contaminated waters [10]. Various adsorbents have been shown to be effective at removing tetracycline, including activated carbon (AC), carbon nanotubes and bentonite [11, 12]. However, these materials are expensive and lower cost alternatives are sought, particularly for large scale water treatment operations [13].

The pyrolysis of biomass yields biochar, which with its porous structure and medium-to-high surface area is similar to AC [14, 15]. The biochar surface contains a non-carbonized fraction that includes O-containing carboxyl, hydroxyl and phenolic functional groups, which can immobilize contaminants [16, 17]. Biochar sorbents have been shown to be an efficient and cost-effective means of removing antibiotic components including, tetracycline, sulfonamides, and ceftiofur from aqueous environments [18–21]. Liu et al. [21] reported the adsorption capacity for tetracycline of biochar derived from rice husks was 17 mg/g for batch experiments where tetracycline concentrations ranged from 50 to 1000 mg/L. However, the adsorption capacity of biochar depends on the biomass feedstock and the pyrolysis process because these factors influence biochar characteristics such as surface area, surface functional groups and porosity [19, 21, 22]. Other work has investigated the impact of the pH of the solution and the ionic strength of the biochar on antibiotics adsorption [21, 23]. However, little work assessing the adsorption of tetracycline on biochar produced under different temperature conditions has been reported.

Rice straw is one of the most abundant agricultural wastes in China [24]. Adopting this low cost, high carbon and abundant biochar feedstock could also decrease the amount that is currently burned, which is a contributor to local air pollution [25, 26]. Our objectives in this work are: 1) to investigate the characteristics of biochar derived from rice straw and its ability to adsorb tetracycline; 2) use adsorption isotherms and thermodynamic analysis to analyze the mechanism by which tetracycline and the biochar interact; and 3) study the effect of pH on the adsorption processes.

Materials and methods

Source materials

The rice straw was obtained from cropland in Hangzhou, Zhejiang province, China. Biochars were produced by pyrolyzing dried rice straw at three different temperatures (300, 500, and 700˚C, yielding the R300, R500, and R700 samples, respectively). The pyrolysis temperature was raised at a rate of 26˚C/min to the target temperature and then held for 2h. Once cool, the biochar samples were ground until they passed through a 0.15mm sieve.

The rice straw was the left over waste having no use for the farmers, and we have obtained permission from the farmer of this private cropland. We confirm that the field studies did not involve endangered or protected species.

The sorbate tetracycline (> 97.7% purity) was purchased from Dr Ehrenstorfer (Ausberg, Germany) while all other chemicals were analytical grade or better.

Biochar characteristics

The biochar samples’ content of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) were analyzed in triplicate with an elemental analyzer (Vario MICRO, Elementar, Germany). The
Brunauer–Emmett–Teller surface area ($S_{\text{BET}}$), total pore volume ($V_{\text{tot}}$), and pore size distribution of the biochar samples were analyzed in triplicate using N$_2$ adsorption at 77 K with an Autosorb–IQC gas analyzer (Quantachrome, USA). Functional groups in the biochar samples were determined using Fourier transform infrared (FTIR) spectrometry (VERTEX 70, BRUKER, Germany).

**Adsorption experiments**

The tetracycline adsorption experiments were carried out in a batch adsorption mode. A stock solution of tetracycline (100 mg/L) was prepared with Milli-Q water and methanol where the concentration of methanol was < 0.1% to minimize the potential co-solvent effects on sorption process [23]. Sorption isotherms were obtained across a tetracycline concentration range of 0.5 to 32 mg/L at temperatures of 15, 25 and 35˚C. Solutions of 60 mg biochar and 20 ml tetracycline were added to 40-ml brown glass vials, which were fitted with a plastic cap. The vials were then shook at 150 rpm for 24 h in a constant temperature oscillator to reach an equilibrium state. Following being shaken, the samples were centrifuged at 5000 rpm for 10 min with the supernatant then filtered through a 0.45-μm membrane. The concentration of tetracycline in the supernatant was measured by high performance liquid chromatography (e2695, Waters, USA) using a C-18 column and a UV–vis spectrometer (2489, Waters, USA) operating at wavelength of 355 nm. A control sample (without biochar) was simultaneously prepared to assess any loss of tetracycline during the sorption process. However, no measurable change was observed for the tetracycline concentrations during the control experiment. All of the experiments were performed in triplicate.

The effect of changing the pH on the adsorption of tetracycline by biochar was determined in another series of batch experiments using a concentration of tetracycline of 32 mg/L. The solution pH was adjusted by using 0.1 mol/L HCl or NaOH to 2.0, 3.5, 5.5, 7.5 and 10.0. A weighed amount of biochar (60 mg) was added to 20 mL tetracycline solution. The experiments were again performed in triplicate.

**Data analysis**

The Langmuir (Eq (1)) and Freundlich (Eq (2)) adsorption models were used to fit the experimental data.

**Langmuir:**

\[
q_e = \frac{q_{\text{max}}K_L C_e}{(1 + K_L C_e)} \tag{1}
\]

**Freundlich:**

\[
q_e = K_f C_e^n \tag{2}
\]

where $q_e$ (mg/kg) is the rate of sorption of tetracycline on the biochar, $C_e$ (mg/L) is the tetracycline concentration in the solution phase, $K_L$ (L/mg) is the Langmuir sorption coefficient, $q_{\text{max}}$ (mg/kg) is the sorption capacity, and $K_f$ (mg$^{1-n}$/L$^n$/kg) and $n$ are the sorption and nonlinear coefficients in the Freundlich equation, respectively.

The efficiency with which a sample removed tetracycline ($R$) was calculated using Eq (3):

\[
R = \frac{C_0 - C_e}{C_0} \times 100\% \tag{3}
\]

where $C_0$ is the initial tetracycline concentration in the solution phase.
Eqs (4–6) were then used to calculate the change in the standard Gibbs free energy ($\Delta G$), enthalpy ($\Delta H$) and entropy ($\Delta S$) [22]:

$$\Delta G = -RT \ln K_d$$  \hspace{1cm} (4)

$$\Delta G = \Delta H - T \Delta S$$  \hspace{1cm} (5)

$$\ln K_d = -\Delta H / RT + \Delta S / R$$  \hspace{1cm} (6)

where $K_d = q_d / C_s$ and represents the sorption coefficient, $T$ (K) is the absolute temperature and $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant. When $\ln K_d$ is plotted against $1/T$, a straight line with a slope of $-\Delta H / R$ and an intercept of $\Delta S / R$ is obtained.

Statistical analysis was performed by SPSS 16.0 (Chicago, IL). For $\Delta G$ values, a two-way ANOVA was applied to examine the effects of pyrolysis and adsorption temperature, the significant differences among treatments were compared with the Tukey’s test at each initial tetracycline concentration (S1 Table). For $\Delta S$ and $\Delta H$ values, a one-way ANOVA was applied to examine the effects of pyrolysis temperature, the significant differences were also tested using Tukey’s test (S1 Table). In order to investigate how chemical properties and pore structure of biochars influence the biochar sorption, correlation analysis ($n = 9$) was used to examine the relationship between biochar characteristics and the $q_e$ values obtained at each initial tetracycline concentration at 25˚C.

**Results and discussion**

**Biochar characteristics**

The chemical properties of the biochar samples derived from rice-straw are shown in Table 1. The O and H content of the samples decreased rapidly as the pyrolysis temperature was increased. Meanwhile, the C content increased from 45.2% for a pyrolysis temperature of 300˚C to 56.0% when the temperature was 700˚C. The ratios of O/C, H/C and (O+N)/C exhibited a similar trend to that of the biochar’s O content. All of these findings were consistent with those reported in previous studies [27]. The fact that lower O/C ratios were observed for samples that were pyrolyzed at higher temperatures indicated that these biochars likely had less hydrophilic surfaces [16]. Taken together, these changes in the chemical composition of the biochar samples indicated that the higher pyrolysis temperatures promoted a higher degree of carbonization.

The surface area ($S_{BET}$) of the biochar samples increased dramatically with temperature (from 2.48 m$^2$/g in R300 to 27.66 m$^2$/g in R700), showing the same trend as the pore volume (as shown in Table 2), both of which were in agreement with previous work [22]. From the FTIR analysis (Fig 1), the peaks at 2922 and 2853 cm$^{-1}$ reflected the presence of aliphatic–CH, while the absorption at 3429 cm$^{-1}$ was assigned to surface–OH groups [21]. The peaks at these

| Biochar | C* (%) | N (%) | O (%) | H (%) | O/C | H/C | (O+N)/C |
|---------|--------|-------|-------|-------|-----|-----|---------|
| R300    | 45.22±0.46 | 1.47±0.06 | 23.41±0.35 | 4.94±0.13 | 0.52 | 0.11 | 0.55   |
| R500    | 52.60±1.06 | 1.35±0.04 | 15.57±0.24 | 2.15±0.07 | 0.30 | 0.04 | 0.32   |
| R700    | 56.00±0.87 | 1.18±0.04 | 11.38±0.10 | 1.29±0.09 | 0.20 | 0.02 | 0.22   |

*The content of C, N, O and H elements in the biochar.*

https://doi.org/10.1371/journal.pone.0182776.t001
three wavenumbers were smaller for the biochar pyrolyzed at 700˚C, which indicated that
increasing the pyrolysis temperature decreased the content of O-containing and aliphatic car-
bon functional groups. Adsorptions in the region 1000 to 1100 cm\(^{-1}\) were ascribed to Si–O–Si
groups, the P–O bond of phosphate and the C–O bond of carbonate [28]. All of these showed
the strongest adsorptions in the R700 samples, indicating the highest mineral salt content
occurred in the sample with the highest pyrolysis temperature.

Tetracycline sorption

The sorption isotherms of tetracycline on the biochar samples are shown in Fig 2. The ad-
sorption data showed a good fit to both the Langmuir and the Freundlich models with \(R^2\) co-
efficients higher than 0.919 in the experimental concentration ranges (as shown in Table 3).
For the parameters in the Freundlich model, the values of \(n\) for the different samples were
similar (0.53–0.62) and less than 1, which indicated that the adsorption was a concentration
dependent process. The value of \(K_f\), which reflects a sample's ability to absorb tetracycline,
was highest in the biochar produced by the 700˚C pyrolysis. The trend shown by the \(q_{\text{max}}\) val-
ues in Langmuir model also suggested that sorption capacity increased with pyrolysis tempera-
ture. The maximum adsorption capacities were calculated to lie in the approximate range of
11,834–14,157 mg/kg.

Table 2. Pore structure of biochars derived from rice straw.

| Biochar | \(S_{BET}\) \((m^2/g)\) | \(V_{\text{tot}}\) \((cm^3/g)\) | Pore width (nm) |
|---------|-----------------|------------------|-----------------|
| R300    | 2.48±0.84       | 0.048±0.008      | 17.06±1.01      |
| R500    | 10.18±1.52      | 0.057±0.011      | 15.27±1.20      |
| R700    | 27.66±4.64      | 0.059±0.010      | 21.55±2.58      |

\(a\)The \(S_{BET}\) and \(V_{\text{tot}}\) represent the Brunauer–Emmett–Teller surface area and total pore volume respectively.

https://doi.org/10.1371/journal.pone.0182776.t002

Fig 1. Fourier transform infrared (FTIR) spectroscopic analysis of biochars derived from rice straw.

https://doi.org/10.1371/journal.pone.0182776.g001
Fig 2. Sorption isotherms for tetracycline on biochars. The adsorption temperatures were (A) 15°C, (B) 25°C and (C) 35°C.

https://doi.org/10.1371/journal.pone.0182776.g002
Surface area is known to be an important factor that influences the adsorption capacities of biochar, and specifically in the case of tetracycline removal [21, 29]. This was confirmed in this study, the surface area ($S_{\text{BET}}$) of the biochar samples was positively correlated with $q_e$ values (Table 4). The adsorption capacities increased as the biochar samples’ surface area increased following exposure to higher pyrolysis temperatures.

The properties of the antibiotic and the biochar affect the adsorption process and the various underlying mechanisms, which include electrostatic, hydrophobic, hydrogen bond and π-π electron-donor acceptor (EDA) interactions [19, 30]. Previous studies have shown that electrostatic interaction (cation and anion attractions) and hydrophobic interaction do not dominate the adsorption of tetracycline on biochar [19, 21]. Under the conditions in this study (pH = 5.5), tetracycline presented as a zwitterion. Thus, although the net charge of tetracycline was neutral, the negative and positive charges were spatially separated within the tetracycline molecule, and acted independently during the adsorption processes [31]. The pH of the isoelectric point of the biochar samples inferred from previous study was lower than that of the solution [32], suggesting that the surface of the biochar samples was negatively charged. Therefore, it is unlikely that hydrophobic interaction or electrostatic interaction (cation and anion

### Table 3. Langmuir and Freundlich model parameters for tetracycline sorption on biochars derived from rice straw at different adsorption temperatures (T).

| Biochar | T (°C) | $K_L$ (10^5 mg·L^-1 kg^-1) | $n$ | $R^2$ | $q_{\text{max}}$ (10^5 mg·L^-1) | $K_L$ (L·mg^-1) | $R^2$ |
|---------|-------|-----------------|-----|------|-------------------------------|----------------|-----|
| R300    | 15    | 0.364±0.034     | 0.62±0.03 | 0.975 | 3.889±0.244                | 0.07±0.01 | 0.984 |
|         | 25    | 0.486±0.040     | 0.58±0.03 | 0.976 | 4.136±0.158                | 0.10±0.01 | 0.992 |
|         | 35    | 0.593±0.068     | 0.54±0.04 | 0.947 | 4.147±0.282                | 0.13±0.02 | 0.965 |
| R500    | 15    | 1.141±0.121     | 0.62±0.05 | 0.953 | 8.384±0.734                | 0.14±0.03 | 0.966 |
|         | 25    | 1.930±0.120     | 0.54±0.05 | 0.937 | 8.756±1.159                | 0.26±0.10 | 0.925 |
|         | 35    | 3.484±0.234     | 0.53±0.04 | 0.938 | 11.695±0.730               | 0.49±0.07 | 0.952 |
| R700    | 15    | 2.301±0.249     | 0.58±0.06 | 0.919 | 11.834±1.417               | 0.23±0.06 | 0.938 |
|         | 25    | 4.817±0.289     | 0.60±0.06 | 0.931 | 14.157±1.522               | 0.71±0.18 | 0.946 |
|         | 35    | 7.307±0.333     | 0.54±0.05 | 0.930 | 13.849±1.359               | 1.61±0.42 | 0.942 |

https://doi.org/10.1371/journal.pone.0182776.t003

### Table 4. Pearson’s linear correlation coefficients between biochar characteristics and the $q_e$ values obtained at different initial tetracycline concentration($C_0$) at 25°C (n = 9).

| $C_0$(mg/L) | C | N | O | H | O/C | H/C | (O+N)/C | $S_{\text{BET}}$ ($\text{m}^2$·g^-1) | Vtot | Pore width |
|-------------|---|---|---|---|-----|-----|---------|---------------------------------|------|------------|
| 0.5         | 0.925** | -0.751** | -0.923** | -0.962** | -0.944** | -0.969** | -0.943** | 0.690* | 0.655 | 0.186 |
| 1.0         | 0.954** | -0.849** | -0.978** | -0.974** | -0.979** | -0.971** | -0.979** | 0.843** | 0.701* | 0.439 |
| 2.0         | 0.965** | -0.802** | -0.957** | -0.984** | -0.974** | -0.990** | -0.973** | 0.758* | 0.656 | 0.280 |
| 4.0         | 0.938** | -0.783** | -0.933** | -0.973** | -0.952** | -0.979** | -0.952** | 0.717* | 0.648 | 0.225 |
| 8.0         | 0.957** | -0.844** | -0.969** | -0.988** | -0.979** | -0.990** | -0.978** | 0.793* | 0.676* | 0.340 |
| 16.0        | 0.962** | -0.948** | -0.989** | -0.971** | -0.980** | -0.962** | -0.981** | 0.941** | 0.669 | 0.609 |
| 24.0        | 0.987** | -0.899** | -0.993** | -0.986** | -0.994** | -0.983** | -0.994** | 0.876** | 0.627 | 0.473 |
| 32.0        | 0.977** | -0.929** | -0.997** | -0.985** | -0.993** | -0.979** | -0.993** | 0.902** | 0.648 | 0.530 |

*Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

The content of C, N, O and H elements in the biochar.

$S_{\text{BET}}$ and $V_{\text{tot}}$ represent the Brunauer–Emmett–Teller surface area and total pore volume respectively.

https://doi.org/10.1371/journal.pone.0182776.t004
attractions) played a dominant role in the adsorption process in the current work. The FTIR analysis indicated that R300 possessed more O-containing functional groups, which can serve as H-bond acceptors. However, the fact that R300’s adsorption capacity was the lowest of all of the samples which suggested that hydrogen bond interactions also did not play a dominant role in the adsorption process.

Conversely, EDA interactions have been reported to be one of the main mechanisms controlling biochar’s adsorption of tetracycline and other molecules [19, 23, 33]. The biochar samples in this work possessed a graphite-like structure which can act as a π-electron-donor [11]. Meanwhile, tetracycline can serve as an π-electron-acceptors thanks to its aromatic ring structure. In this study, $q_e$ values were positively correlated with the content of C in the biochar (Table 4). As the pyrolysis temperature was increased, the degree of graphitization of biochar increased, thus enhancing the sample’s adsorption capacity.

**Tetracycline adsorption capacity and removal efficiency**

The calculated efficiencies with which the biochar samples removed tetracycline are presented in Fig 3. The R500 and R700 samples showed relatively high removal efficiencies with the highest (92.8–96.7%) calculated for the R700 sample for adsorption at 35˚C. The tetracycline adsorption capacity of various materials has been reported to follow the following order: carbon nanotubes $>$ AC $>$ bentonite [10, 11, 34]. The adsorption capacities of the samples in this work (which maximum 14.16 mg/g) were lower than those reported for AC (typically 100–1000 mg/g) [11, 35], but higher than those of clay, soil and rice husk ash [13, 36, 37]. The removal efficiencies, particularly those of the samples pyrolyzed at higher temperatures, were similar to those observed for AC (74–88% for a tetracycline concentration of 20 mg/L) [34]. Taken together, the results suggest that biochar derived from rice straw appears to be a useful means of treating tetracycline-contaminated water.

**Thermodynamics analysis**

Analysis of the thermodynamics of the sorption process can help to illustrate the underlying mechanisms and the impact on them of the adsorption temperature. Fig 4 showed the relationship between $\ln K_d$ and $1/T$. The $\Delta G$ values calculated from $\ln K_d$. Negative $\Delta G$ values were detected for all samples (S1 Table, Table 5). This suggested, in agreement with previous studies [13, 38], that the sorption of tetracycline on biochar derived from rice straw was thermodynamically favorable and spontaneous for all of the pyrolysis temperatures investigated. The increase in the magnitude of $\Delta G$ with the temperature of the sorption environment (S1 Table,
Table 5) indicated that the tetracycline sorption process was more thermodynamically favorable at higher sorption temperatures. Unlike the sorption of sulfamethoxazole on biochar [22], the magnitude of ΔG increased with the pyrolysis temperature, again suggesting that increased temperature (this time during the biochar preparation) yielded a more thermodynamically favorable sorption process. At same time, the ΔG values of adsorption processes in this work were higher than those reported for graphene oxide (from -3.27 kJ/mol to -2.01 kJ/mol) [39] and multi-walled carbon nanotubes (from -5.54 kJ/mol to -3.99 kJ/mol) [40] but lower than those of activated carbon nanoparticles (from -87.97 kJ/mol to -82.60 kJ/mol) [34].

The ΔH values for the various samples ranged from 11.05 to 91.27 kJ/mol (S1 Table, Table 5) indicating that the overall process was endothermic. This finding also suggested that the adsorption process was more favorable at higher temperatures, which is consistent with the trend in adsorption capacities described in Table 2. This result may be due to the increase in diffusion rate of tetracycline as the temperature increases. An increased number of tetracycline molecules may also acquire sufficient energy to interact with active sites on the surface of the biochar [41]. The trend in ΔS was similar to that for ΔH, with the positive ΔS values
revealing that the adsorption process was favored sorption stability [42]. As $\Delta S$ increased with the pyrolysis temperature (S1 Table), this indicated randomness increased at the tetracycline–biochar interface during the adsorption process [13]. The net positive entropy may be attributed to that the positive entropy change caused by the changes in the surface of the biochar exceeds numerically the negative entropy change result from loss of freedom of the tetracycline [43]. Compared to some other carbon-material, the $\Delta H$ and $\Delta S$ values in this study were lower than those reported for activated carbon nonoparticles [34] but higher than those reported for multi-walled carbon nanotubes [40]. As to graphene oxide, only the R700 exhibit higher $\Delta H$ and $\Delta S$ values compared to graphene oxide [39].

### The impact of pH

The adsorption capacity for different biochar samples under various pH conditions are shown in Fig 5. For all pH conditions, tetracycline adsorption capacity increased with pyrolysis temperature. For all samples, as pH was increased, the samples’ adsorption capacity initially increased but then fell, which was consistent with previous studies [23]. The pH of the solution influenced the adsorption processes by changing the surface charges of the biochar and tetracycline [21, 23]. Tetracycline is amphoteric and depending on the pH can be a cation (pH < 3.3), a zwitterion (3.3 < pH < 7.7) or an anion (pH > 7.7) [42]. Previous studies evaluated the isoelectric point of biochar derived from rice straw to be between 3 and 4 [32, 44]. Thus, when the solution pH was 2, the biochar surface was positively charged. However, increasing the pH caused the biochar’s surface to become negatively charged. Electrostatic repulsion occurred when the pH was outside of the range of 3.3–7.7, which resulted in decreased adsorption capacities at these pH values.

### Conclusions

This study showed the biochars pyrolyzed at 500 and 700˚C were relatively high efficient at removing tetracycline from an aqueous solution. The high adsorption capacity for the R700 sample was attributed to the relatively high surface area and EDA interactions between the tetracycline molecules and the biochar’s graphitic surfaces. A thermodynamic analysis indicated that adsorption of tetracycline on biochar was thermodynamically favorable and spontaneous, and that $\Delta H$ and $\Delta S$ increased with pyrolysis temperature. The pH of the solution also influenced the adsorption processes with a maximum adsorption capacity occurring at pH = 5.5.

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**Table 5. Thermodynamic parameters for tetracycline sorption on biochars with initial concentration of tetracycline changing from 0.5 mg/L to 32 mg/L.**

| Biochar | Temperature(˚C) | Thermodynamic parameters | ΔG (kJ/mol) | ΔH (kJ/mol) | ΔS (J/(mol K)) |
|---------|----------------|-------------------------|-------------|-------------|----------------|
| R300    | 15             | -14.17–11.17<sup>a</sup> | 11.05–37.76 | 81.85–174.06 |
|         | 25             | -15.40–11.99            |             |             |                |
|         | 35             | -17.05–12.64            |             |             |                |
| R500    | 15             | -17.08–14.47            | 44.64–76.10 | 204.80–323.43 |
|         | 25             | -21.43–16.10            |             |             |                |
|         | 35             | -23.55–18.59            |             |             |                |
| R700    | 15             | -18.99–16.16            | 52.85–91.27 | 282.14–378.80 |
|         | 25             | -22.94–20.11            |             |             |                |
|         | 35             | -25.24–22.52            |             |             |                |

<sup>a</sup>Minimum–Maximum.
Overall, biochar derived by pyrolyzing rice straw offers a promising option for a low-cost method of removing tetracycline from water and could be used to mitigate tetracycline pollution of wastewater from livestock farms. However, it is important to clarify that this study was based on aqueous solution, the matrix of wastewater is relatively complex and so the practical application need further investigation.

Supporting information

S1 Table. Thermodynamic parameters for tetracycline sorption on biochars at different initial concentration of tetracycline ($C_0$).

Author Contributions

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