Removal of amoxicillin from aqueous solution using sludge-based activated carbon modified by walnut shell and nano-titanium dioxide

Xiaorong Kang, Yali Liu, Can Yang and Han Cheng

ABSTRACT

Dewatered municipal sludge was used as raw material to prepare activated carbon (SAC), and the SAC was modified by walnut shell and nano-titanium dioxide (MSAC). The results showed that the MSAC had a higher specific surface area ($S_{BET}$) (279.147 m$^2$/g) and total pore volume ($V_T$) (0.324 cm$^3$/g) than the SAC. Simultaneously, the functional groups such as C-O, C = O, and Ti-O-Ti on the surface of MSAC were enhanced due to modification. These physicochemical properties provided prerequisites for the diffusion and degradation of pollutants in MSAC. Furthermore, the MSAC was applied to adsorb amoxicillin (AMX) from aqueous solution, in batch experiments, the maximum removal rate (88.19%) was observed at an initial AMX concentration of 30 mg/L, MSAC dosage of 5.0 g/L, pH of 8, contact time of 180 min, and temperature of 25 °C. In addition, the adsorption process was well described by the Freundlich isotherm model and pseudo-second-order kinetic model, indicating that the adsorption of AMX onto MSAC was dominated by multilayer chemisorption. Also, the adsorption thermodynamics suggested that the adsorption process of AMX onto MSAC was endothermic, feasible and spontaneous.

Key words | activated carbon, adsorption kinetics, amoxicillin, dewatered sludge, modification

HIGHLIGHTS

- Sludge-based activated carbon was modified by walnut shell and nano-TiO$_2$.
- Above 88% of amoxicillin was removed.
- Optimum operational parameters were determined.
- Adsorption process was dominated by multi-layer chemisorption.

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INTRODUCTION

Sludge is an unavoidable by-product of biological treatment in wastewater treatment plants (WWTPs). In 2016, approximately 13 million tons of dry sludge was produced in China (Liu et al. 2017b). As sludge contains a large amount of heavy metals, organic pollutants and pathogenic microorganisms, traditional methods for sludge treatment such as landfill, incineration and land application pose huge threats to the environment, economy and human health (Chitongo et al. 2013; Wang et al. 2013). In recent years, based on the advantages of cheapness, availability, and high organic contents, sludge used as raw material to prepare activated carbon (AC) has been regarded as a sustainable approach of sludge management (Devi & Saroha 2017). Simultaneously, the sludge-based AC (SAC) has been attempted to remove various pollutants such as heavy metals, dyes, and pharmaceuticals from aqueous solution or wastewater (Jin et al. 2016; Jaria et al. 2019a; Sullivan et al. 2019).

Antibiotics have been listed as an important part of emerging organic pollutants, and their pollution to the aquatic environment has become a great concern (Gonzalez-Pleiter et al. 2013). As previously reported, continuous discharge of antibiotics into the aquatic environment may have toxic effects on non-target individuals (Gonzalez-Pleiter et al. 2013), and their persistence and bioaccumulation also induce long-term risks to aquatic organisms and human health (Kumari & Kumar 2020). For these reasons, tremendous efforts have been made to remove antibiotics from water or wastewater (Silva et al. 2018; Li et al. 2019c). Among various treatment methods, adsorption is still considered to be the best way to treat antibiotic wastewater, and SAC has shown great potential in removing selected antibiotics (Yang et al. 2016; Jaria et al. 2019b; Silva et al. 2019). Compared with commercial AC, the AC produced from paper mill sludge (PS-AC) exhibited faster adsorption kinetics (15–30 min) for sulfamethoxazole (SMX) (Calisto et al. 2015). Chowdhury et al. (2019) also demonstrated that the PS-AC effectively adsorbed enrofloxacin (ENF) from solution (95.85%) at an initial concentration of 12 mg/g, an adsorbent dosage of 1.2 g/L, and a contact time of 18 h. In addition, Yao et al. (2013) comparatively studied the adsorption effect of sludge source on gatifloxacin (GAT), and the results showed that all SACs had high adsorption capacity for GAT except that made from dried sludge. However, there is scarcity of research concerning the removal of amoxicillin (AMX) using AC prepared from municipal sludge. This may be because high contents of ash and inorganics in the municipal sludge mask the active adsorption sites, resulting in a weak adsorption capacity for organic contaminants (Li et al. 2016).

Therefore, the physical and chemical characteristics of SAC should be modified to improve its adsorption capacity (Devi & Saroha 2017). Various agricultural and forestry residues are reported to be much better carbon-rich biomass materials than municipal sludge, containing more lignin and cellulosics, and lower ash (Li et al. 2016). They are usually,
therefore, added into sludge to prepare AC samples with large specific surface areas, well-developed pore structures, and strong aromatic groups, which have excellent adsorption capacities for organic pollutants in aqueous solution (Yu et al. 2019). On the other hand, the combined use of biochar with nanometallic oxides had high removal capacities for pharmaceuticals (Li et al. 2019b; Hassan et al. 2020). Some literatures showed that the biochar modified with titanium dioxide (TiO2) exhibited much higher specific surface area, which increased the interaction between photocatalytic active sites and absorbates (Fazal et al. 2019; Li et al. 2019a; Silvestri et al. 2019). Recently, Li et al. (2019a) found that the ultrafine nano-TiO2 was incorporated into chicken feathers to synthesize light-recycling biochar, and its removal rate for AMX reached 99.97%.

Based on the above research, the main purpose of this study is to evaluate the feasibility of combined modification of walnut shell and nano-TiO2 for SAC, and the modified SAC (named MSAC) was used to remove AMX from aqueous solution. The MSAC was physically and chemically characterized by scanning electron microscopy (SEM) and Fourier Transform Infrared Spectrometer (FTIR), respectively. Then, the MSAC was tested in batch experiments for the adsorption of AMX, and the effects of five operational parameters, including initial AMX concentration, MSAC dosage, pH, temperature, and contact time, on removal rates were studied. In addition, kinetic models and adsorption isotherm models were investigated to analyze the adsorption mechanism of AMX onto MSAC.

**MATERIALS AND METHODS**

**Raw materials**

The dewatered municipal sludge (DMS) used in this test was taken from Qiaobei WWTP in Nanjing, China. Its water content was 79.43%, and the dry weight of volatile solids (VS), ash, C, H, and N were 61.48, 38.52, 25.90, 6.43 and 4.11%, respectively. The walnut shell was purchased from a food company in Nanjing, China. Its characteristics were as follows: VS 98.16%, ash 1.84%, water content 3.57%, C 48.27%, H 6.51% and N 0.34%. These raw materials were dried to constant weight at 105 °C with a drying oven (DGG-9030A, Donglu, Shanghai, China), respectively, and then crushed and sieved through a 40-mesh sieve.

**Chemicals**

In this study, chemical activating agent ZnCl2 was analytically pure, and the purities of HCl and NaOH were 37 and 96%, respectively. They were provided by Nanjing Chemical Reagent Co. Ltd, Nanjing, China. High-purity nano-TiO2 and AMX were purchased from Shanghai Mack-Lin Biochemical Technology Co. Ltd, Shanghai, China.

**AMX stock solution preparation**

A stock solution with concentration of 200 mg/L was prepared by dissolving 0.2 g AMX into 1,000 mL ultra-pure water. Other AMX concentrations required in the experiment were obtained by diluting the stock solution with ultra-pure water.

**Preparation of AC samples**

In the first step, according to the experimental data (Supplementary material, Figure 1S), the walnut shell, DMS, and nano-TiO2 were thoroughly mixed in a stainless-steel reactor with a mass ratio of 16:24:1, and then activated with 5.0 M of ZnCl2 solution, the final solid–liquid ratio was 1:3. Second, the mixture was shaken in a thermostatic shaker incubator (SHZ-82, Guohua, Changzhou, China) for 24 h at 25 °C. After shaking, the mixture was centrifuged at 2,352×g for 5 min, and the sediment was dried in a drying oven at 105 °C to constant weight. Third, the dried mixed solid was pyrolyzed in N2 atmosphere at 550 °C for 30 min in a resistance furnace (SX-12-10, Xinyi, Shanghai, China), and then cooled to room temperature overnight. Next, the product was washed with 1.0 M HCl, and rinsed with ultra-pure water to neutral pH value. Finally, the prepared MSAC was crushed, ground and sieved to obtain a particle size less than 40 mesh.

**Adsorption tests**

A series of adsorption studies were conducted in batch mode. The effects of initial AMX concentration (10–90 mg/L), MSAC
or SAC dosage (1–8 g/L), pH (4–10), contact time (15–180 min), and temperature (15–40 °C) on the adsorption capacity of AMX were studied. In each experiment, only one parameter was changed, and other parameters remained constant. After stirring for a predetermined time interval, 4 mL sample was taken and filtrated through 0.45 μm cellulose acetate membrane (Newstar, Hangzhou Special Paper Industry Co. Ltd, Hangzhou, China), and then the residual AMX concentration in the filtrate was analyzed. The pH values were adjusted by 1.0 M NaOH or HCl solution.

For kinetic studies, 5 g/L of MSAC and SAC were placed in 250 mL Erlenmeyer flasks and contacted with 100 mL of AMX solution (30 mg/L), respectively. The solutions were shaken for different time intervals within 0–180 min. The removal rate (E, %) and the adsorption capacity (qe, mg/g) of AMX at time t, were calculated by Equations (1) and (2):

\[ E = \frac{C_0 - C_t}{C_0} \times 100\% \]  
\[ q_t = \frac{(C_0 - C_t)V}{W} \]  

where \( C_0 \) (mg/L) is the initial concentration of AMX (mg/L), and \( C_t \) (mg/L) represents the AMX concentration at time t. \( V \) (L) is the volume of AMX solution, and \( W \) (g) is the weight of MSAC or SAC.

Adsorption isotherm was performed at an MSAC or SAC dosage of 5 g/L and 25 °C by varying initial AMX concentrations (10–90 mg/L). The adsorbed amount of AMX onto MSAC or SAC at the equilibrium, \( q_e \) (mg/g), was calculated by Equation (3):

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

where \( C_e \) (mg/L) is the equilibrium concentration of AMX.

All tests were repeated three times, and the average and standard deviation values were recorded.

### Analysis methods

The VS, ash and water content were measured according to Standard Methods (APHA 2001). The analysis of AMX concentration referred to previous literature (Baere & Backer 2007). The pH values were measured using a pH meter (PHS-3C, Leici, Shanghai, China). The elemental compositions of DMS and walnut shell (C, H and N) were analyzed by an automatic elemental analyzer (Vario EL cube, Elementar, Hanau, Germany).

The porosity and surface area characterization of MSAC and SAC were measured by a surface area analyzer (Micrometrics, ASAP2020, Norcross, GA, USA). The surface morphology was observed with a SEM (QUANTA 200, FEI, Hillsboro, OR, USA). The surface functional groups on MSAC and SAC were evaluated by a FTIR spectrometer (IR-360, Nicolet, Madison, WI, USA) with a wavelength range of 400–4,200 cm\(^{-1}\).

### Results and Discussion

#### Characteristics of AC samples

**Physical characterization**

The N\(_2\) adsorption/desorption isotherms of SAC and MSAC are shown in Figure 1. It is evident that the isotherm shapes of SAC and MSAC were classified as Type II according to the International Union of Pure and Applied Chemistry (IUPAC) classification (Zhang et al. 2016). At \( p/p_0 < 0.01 \), the N\(_2\) adsorption capacity (63.4 cm\(^3\)/g) of MSAC was much higher than SAC (8.9 cm\(^3\)/g), indicating that MSAC possessed more micropores (Pal et al. 2017). Then, an increase in N\(_2\) adsorption volume was observed with the increase of \( p/p_0 \), showing the multilayer adsorption occurred on the outer surfaces of SAC and MSAC (Wang et al. 2016). Meanwhile, the hysteresis loops appearing at \( p/p_0 > 0.4 \) should be attributed to the capillary condensation phenomenon of mesopore structure in SAC and MSAC (Liu et al. 2017a).

The pore structure parameters of SAC and MSAC were also analyzed in this study. The specific surface area (\( S_{\text{BET}} \)) and total pore volume (\( V_p \)) of MSAC were 279.147 m\(^2\)/g and 0.324 cm\(^3\)/g, respectively, which were significantly superior to SAC (35.921 m\(^2\)/g and 0.097 cm\(^3\)/g). In addition, the average pore size (\( D_p \)) of MSAC (4.495 nm) was smaller than SAC (10.425 nm), and the corresponding micropore volume (\( V_{\text{mic}} \)) of MSAC (0.045 cm\(^3\)/g) was more than 11 times that of SAC.

The surface morphology of SAC and MSAC was analyzed by SEM (Figure 2). In comparison to SAC, the
surface of MSAC exhibited more irregular and looser texture, which also illustrated its large $S_{\text{BET}}$ and high porosity. To some extent, the differences between SAC and MSAC explained the effect of combined modification on the formation of porous structures.

In summary, these physical parameters of MSAC revealed that the mesoporous structure provided more channels for AMX to enter the micropores. Simultaneously, the AMX molecules could penetrate into the interior of micropores, because the AMX molecule size is only about 13 Å, which is smaller than the $D_p$ of MSAC.

**Chemical characterization**

It is reported that the adsorption properties of AC are strongly influenced by its surface functional groups (Salame & Bandosz 2003; Zhang et al. 2016). The spectra for SAC and MSAC are depicted in Figure 3. The very broad peak observed at 3,550–3,200 cm$^{-1}$ evidenced the O-H stretching vibrations for carboxyl and phenol (Anisuzzaman et al. 2016). A band at 1,685 cm$^{-1}$ could be identified to be C=O, which is associated with carboxylic, lactone and other basic oxygen functional groups such as chromones and pyrone (Gokce & Aktaş 2014). The peaks around 1,025 and 1,383 cm$^{-1}$ were derived from the C-O bonds in alcohol and lactone groups, respectively (Gokce & Aktaş 2014). More oxygen-containing functional groups
were found on the MSAC, which were more likely to provide a large number of active sites to interact with AMX. In addition, the peaks around 467 and 746 cm\(^{-1}\) were attributed to the stretching vibration of Ti-O-Ti and bending vibration of Ti-O-C, respectively (Natarajan et al. 2017), which were crucial in promoting photocatalytic degradation of AMX (Li et al. 2019a).

**Removal performances**

**Effect of AC dosages**

The effects of MSAC or SAC dosages (1–8 g/L) on AMX removal were studied at initial AMX concentration, pH, temperature, and contact time of 30 mg/L, 8.0, 25 °C and 180 min, respectively. As shown in Figure 4(a), when the MSAC dosage increased from 1.0 to 5.0 g/L, the removal rate of AMX gradually increased from 41.17 to 88.19%, and then remained relatively stable with the further increase of MSAC dosage. Similarly, AMX removal rate increased from 17.2 to 72.4% at SAC dosages of 1.0–6.0 g/L. In this study, as the dosages of SAC or MSAC increased, the improvement in AMX removal rate was mainly due to the increase in the number of available active sites (Chowdhury et al. 2019). Additionally, the higher removal rates of AMX by MSAC than SAC may be related to the synergistic effect of adsorption and photocatalysis.

**Effect of initial concentrations**

The effects of initial concentrations on AMX removal were conducted by varying AMX concentrations from 10 to 90 mg/L, and other parameters were controlled at pH 8.0, temperature 25 °C, and contact time 180 min. The result is presented in Figure 4(b). The removal rate went up from 73.7 to 88.19% when the initial AMX concentration increased from 10 to 30 mg/L. However, as the initial AMX concentration further increased to 90 mg/L, the removal rate first decreased and then stabilized at 70.8%. The increase in removal rate may be positively related to an enhancement of concentration gradient, which led to an increase in the driving force for adsorption (Chowdhury et al. 2019). In the current research, since the MSAC dosage remained constant during the adsorption process, the number of available active sites and photocatalysts was fixed. When the initial AMX concentration increased to a certain limit, the surface binding sites of MSAC reached saturation resulting in a reduction in AMX removal rate. In addition, SAC had a similar change trend to MSAC, and the removal rate of SAC to AMX at any initial AMX concentration was lower than that of MSAC. It could be speculated that the physical and chemical properties of MSAC were improved through combining modification.

**Effect of pH**

Figure 4(c) shows the effect of pH on AMX adsorption onto MSAC or SAC. It can be found that the initial pH had obvious influences on the removal performance of AMX. Taking MSAC as an example, the removal rates of AMX first increased and then decreased sharply, and the optimum removal rate (88.19%) appeared at pH 8.0. It is also seen from Figure 4(c) that the MSAC showed superior AMX removal rate than SAC at any pH value, indicating that the removal performance of MSAC to AMX was enhanced due to combining modification. The pH 8.0 was selected for the following kinetic, isotherm and thermodynamic experiments.

In this study, the surface charges distribution of AMX or AC samples and the surface property of nano-TiO\(_2\) particles may be affected by strong acid or alkali conditions, which changed the electrostatic interaction and photocatalytic effect of MSAC on AMX. As is reported, the dissociation constants of carboxyl (pK\(_{a1}\)), amino (pK\(_{a2}\)) and hydroxyl (pK\(_{a3}\)) in AMX molecule were 2.68, 7.49 and 9.63, respectively (Goddard et al. 1996). In an acidic environment (pH 2.0–6.0), active groups such as carboxyl, amino and hydroxyl in AMX existed in the forms of -COOH/-COO\(^{-}\), -NH\(_3\)+ and -OH, respectively, which was of benefit for increasing the electrostatic affinity between AMX and AC samples (Pezoti et al. 2016). The reduction of AMX removal rate at pH 10.0 may be attributed to the electrostatic repulsion of AMX molecules by the AC samples, because both carboxyl and amine groups were deprotonated under basic conditions, making AMX negatively charged (Moussavi et al. 2013).

**Effect of contact time**

The effect of contact time on AMX removal was evaluated over a time range of 15–180 min. As shown in Figure 4(d),
Figure 4 | Effect of: (a) AC dosages, (b) initial concentrations, (c) pH, (d) contact time, and (e) temperature on adsorption of AMX onto MSAC. Error bars represent the range of data from duplicate experiments.
the adsorption of AMX onto MSAC reached equilibrium at 60 min. In the first 60 min a sharp increase in AMX removal rate from 55.8 to 84.3% was observed, indicating that the adsorption process of AMX onto MSAC was very fast. However, further increase in contact time after equilibration did not change the removal rate of AMX. This is because there were many available binding sites on the surface of MSAC at the initial stage, nevertheless, with the increase of contact time, MSAC underwent a certain adsorption process, and the active sites were occupied by AMX molecules and reached saturation (Chitongo et al. 2019).

**Effect of temperature**

The effect of temperature on AMX removal was conducted at 15–40 ºC, and the result is shown in Figure 4(e). The removal rate of AMX increased and reached the highest at 25 ºC, and then declined with further increase in temperature. In this study, the maximum removal rate of AMX onto MSAC was 88.19%. This may be due to the fact that the kinetic energy of AMX molecules was low at lower temperatures, leading to the contact between the active sites on the MSAC and the AMX molecules being reduced. At higher temperatures, the kinetic energy of AMX molecules exceeded the attractiveness of MSAC to AMX, resulting in the decrease of removal rates (Chowdhury et al. 2019).

**Adsorption kinetics studies**

The kinetic models, including pseudo-first order (PFO), pseudo-second order (PSO) and intra-particle diffusion (IPD), were used for fitting the experimental data. The linear forms of PFO, PSO and IPD models are determined by Equations (4)–(6), respectively (Siminon 2016):

\[
\ln (q_e - q_t) = \ln q_e - k_1 t \tag{4}
\]

\[
t/q_t = 1/k_2 q_e^2 + t/q_e \tag{5}
\]

\[
q_t = k_{ip}t^{1/2} + C \tag{6}
\]

where \(k_1\) (1/min) and \(k_2\) (g/(mg·min)) are the rate constant of PFO and PSO, respectively. The \(k_{ip}\) ((mg·min\(^{-1/2}\))/g) is diffusion rate constant in particles, and \(C\) is constant.

The fitting results and parameters obtained from the kinetic models are displayed in Figure 5 and Table 1, respectively. It can be seen from Table 1 that the correlation coefficients (R\(^2\)) of SAC and MSAC in the PSO model were 0.9967 and 0.9985, respectively, which were higher than that of the PFO and the IPD models. Meanwhile, the calculated \(q_e\) value (\(q_e^{cal}\)) by PSO model were closer to the experimental \(q_e\) value (\(q_e^{exp}\)). Therefore, these results indicated that the PSO model was more reasonable for describing the adsorption process of AMX onto the SAC and MSAC. According to literature (Guo et al. 2014), the PSO model suggested that the adsorption of AMX onto the MSAC was mainly a chemisorption process. As shown in Table 1, the R\(^2\) values of PFO and IPD models were >0.79, suggesting that the physisorption and intra-particle diffusion may contribute to the adsorption process (Chitongo et al. 2019). The same conclusion was also drawn from Figure 5. In this study, the straight line in Figure 5(c) did not pass through the origin of the coordinate, indicating that there was a certain degree of boundary layer adsorption.

**Adsorption isotherm models**

Adsorption isotherm is very important for the equilibrium and adsorption behavior of adsorbates onto AC samples (Siminon 2016). Therefore, the Langmuir, Freundlich and Temkin isotherm models were used for fitting the experimental results. A linear form of Langmuir equation is expressed as follows:

\[
C_e/q_e = 1/k_L q_m + C_e/q_m \tag{7}
\]

where \(k_L\) (L/mg) is the Langmuir constant related to the adsorption energy, and \(q_m\) (mg/g) is theoretical maximum AMX adsorption amount. The \(q_m\) and \(k_L\) values are deduced from the slope and intercept of the linear plot of \(C_e/q_e\) against \(C_e\), respectively.

The nature of Langmuir isotherm can be further explained by separation factor (\(R_L\)) as given below:

\[
R_L = 1/(1 + k_L C_0) \tag{8}
\]

\(R_L\) is usually used to predict the adsorption efficiency. Adsorption is unfavorable when \(R_L > 1\); favorable when \(0 < R_L < 1\); while \(R_L = 1\) indicates linearity.
The Freundlich isotherm model is used to describe a multilayer adsorption process of adsorbates onto AC samples (Banerjee et al. 2019). A linear form of Freundlich equation is shown in Equation (9):

\[
\ln q_e = \ln k_F + \ln C_e/n \tag{9}
\]

where the \(k_F\) (mg/g·(L/mg)^1/n) is Freundlich constant, and \(n\) is the adsorption intensity. The \(k_F\) and \(n\) are obtained from the slope and intercept of the graph of \(\ln q_e\) versus \(\ln C_e\). When \(n = 1\), the adsorption process is linear; when \(n < 1\), it is basically chemical; when \(n > 1\), it is basically physical (Pezoti et al. 2016).

The Temkin isotherm model is mainly used to describe the electrostatic interaction and related heat between the adsorbates and the AC samples during the chemisorption process. The linear equation of Temkin isotherm is given below:

\[
q_e = \left(\frac{RT}{b_T}\right) \ln k_T + \left(\frac{RT}{b_T}\right) \ln C_e \tag{10}
\]

where \(k_T\) (L/mg) is the Temkin isotherm equilibrium binding constant, and \(b_T\) (J/mol) is the Temkin isotherm constant showing variation of adsorption energy; \(T\) (K) represents the absolute temperature, and \(R\) (J/(mol·K)) is the universal gas constant, 8.314. \(k_T\) and \(b_T\) are determined by the slope and intercept in the plot of \(q_e\) against \(\ln C_e\), respectively.
Figure 6  | (a) Langmuir isotherm, (c) Freundlich isotherm, (e) Temkin isotherm models of AMX onto SAC, and (b) Langmuir isotherm, (d) Freundlich isotherm, (f) Temkin isotherm models of AMX onto MSAC.
The fitted results of the experimental data and the linear models and the corresponding parameters are shown in Figure 6 and Table 2, respectively. Based on the $R^2$ (>0.85) described in Table 2, it is demonstrated that these three models all fitted well with the adsorption processes of AMX onto the MSAC and SAC. It can also be seen that the Freundlich model showed a higher fitting degree than the Langmuir and Temkin models, because the $R^2$ value of Freundlich isotherm was closer to 1. Simultaneously, the $n$ value for AMX adsorption onto the MSAC or SAC was >1, which suggested the adsorption process was multilayered and probably occurred on heterogeneous surfaces (Chowdhury et al. 2019). Moreover, the $q_m$ and $R_L$ of the MSAC, as predicted by Langmuir isotherm, were higher than that of the SAC. In this study, the $q_m$ and $R_L$ values of MSAC were 97.087 mg/g and 0.73, respectively, indicating that the adsorption of AMX onto the MSAC was favorable. The results of $k_T$ and $b_T$ implied that as the surface coverage of MSAC enhanced, the heat of adsorption decreased.

### Adsorption thermodynamics

Thermodynamics studies were evaluated by thermodynamic parameters, including entropy change $\Delta S$ (kJ/mol K), enthalpy change $\Delta H$ (kJ/mol), and Gibb’s free energy change $\Delta G$ (kJ/mol). The $\Delta G$ is determined by Equations (11) and (12) (Mondal et al. 2016):

\[
\Delta G = -RT \times \ln \left( \frac{C_a}{C_e} \right) \quad (11)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (12)
\]

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>SAC</th>
<th>MSAC</th>
</tr>
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<tr>
<td></td>
<td>$k_L$ (L/mg)</td>
<td>0.017</td>
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<td>Langmuir model</td>
<td>$q_m$ (mg/g)</td>
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<td>97.087</td>
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<td></td>
<td>$R_L$</td>
<td>0.658</td>
<td>0.73</td>
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<td></td>
<td>$R^2$</td>
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<td>$k_F$ (L/mg)</td>
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<td>1.103</td>
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<td>$R^2$</td>
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<td>0.9971</td>
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<td></td>
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<td>$b_T$ (L/mol)</td>
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<td></td>
<td>$R^2$</td>
<td>0.9259</td>
<td>0.8828</td>
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Table 2 | Adsorption isotherm parameter of AMX removal by SAC and MSAC

Table 3 | Thermodynamic parameters at different temperatures

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T$(K)</th>
<th>$\Delta G$(kJ/mol)</th>
<th>$\Delta H$(kJ/mol)</th>
<th>$\Delta S$(kJ/(mol·K))</th>
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<tbody>
<tr>
<td>SAC</td>
<td>288.15</td>
<td>1.351</td>
<td>5.334</td>
<td>13.820</td>
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<tr>
<td></td>
<td>293.15</td>
<td>1.283</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>1.214</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSAC</td>
<td>288.15</td>
<td>–0.698</td>
<td>7.497</td>
<td>28.438</td>
</tr>
<tr>
<td></td>
<td>293.15</td>
<td>–0.840</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>–0.982</td>
<td></td>
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</tr>
</tbody>
</table>

where $C_a$ (mg/L) is the AMX concentration on MSAC or SAC in equilibrium. The $\Delta S$ and $\Delta H$ can be calculated from the slope and intercept of the linear plot of $\Delta G$ versus $T$, respectively.

As shown in Table 3, the $\Delta G$ for the sorption of AMX onto SAC was positive, while the $\Delta G$ of MSAC was negative at three adsorption temperatures. The $\Delta G < 0$ meant that the adsorption process of AMX on the surface of MSAC was spontaneous (Bedia et al. 2017). Simultaneously, an increase in the absolute value of $\Delta G$ showed that the spontaneity was enhanced at high temperature. The positive value of $\Delta H$ indicated that the diffusion and adsorption of AMX on MSAC or SAC was an endothermic process (Luo et al. 2017). Furthermore, the positive value of $\Delta S$ also confirmed an increase of randomness at the interface of MSAC and AMX (Chowdhury et al. 2019). In this study, the enhancement of functional groups and the development of pore structures on the surface of MSAC may be the main reasons for the different adsorption parameters of MSAC and SAC.

### CONCLUSIONS

The MSAC was obtained by combining modification of walnut shell and nano-TiO$_2$, and it was applied to adsorb AMX from aqueous solution. The highest AMX removal rate of 88.19% was observed at an MSAC dosage of 5.0 g/L, an initial AMX concentration of 30 mg/L, a temperature of 25 °C, a contact time of 180 min, and a pH of 8.0. The MSAC had better physicochemical properties than SAC in terms of pore structure (especially micropores), and surface functional groups (C-O, C=O, Ti-O-Ti), so it was more favorable for the removal of AMX. The adsorption of AMX onto MSAC fitted well with the PSO kinetic model.
and Freundlich isotherm model. The maximum monolayer adsorption capacity of MSAC (97.087 mg/g) was much higher than that of SAC (30.845 mg/g). In addition, the adsorption thermodynamics study showed the adsorption process was endothermic, feasible and spontaneous.

ACKNOWLEDGEMENTS

This work was financially supported by the Nanjing Forestry University Youth Innovation Fund (CX2017025), National Natural Science Foundation of China (51608272), and Undergraduate Practical Innovation Training Program Project (2019NFUSPITP0487).

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


Guo, X., Du, B., Wei, Q., Yang, J., Hu, L., Yan, L. & Xu, W. 2014 Synthesis of amino functionalized magnetic graphenes composite material and its application to remove Cr(VI), Pb(II), Hg(II), Cd(II) and Ni(II) from contaminated water. J. Hazard. Mater. 278, 211–220.


First received 8 July 2020; accepted in revised form 27 September 2020. Available online 19 November 2020.