Adsorption of methyl orange dye onto biochar adsorbent prepared from chicken manure
Jiangang Yu, Xingwen Zhang, Dong Wang and Ping Li

ABSTRACT
In this work, the biochar adsorbent carboxymethyl cellulose (CMC), was prepared from the pyrolysis (600 °C, 120 min) of chicken manure for the removal of methyl orange (MO) from aqueous solution, and its physicochemical properties were characterized by scanning electron microscopy (SEM) and Fourier transform infrared spectra (FTIR). The experimental parameters including agitation speed, initial solution pH, biochar dosage and contact time on the adsorption properties of MO from aqueous solution onto CMC were investigated in batch experiments. The kinetic adsorption of different initial concentration could be accurately described by the pseudo-second-order model and the overall rate process was apparently influenced by external mass transfer and intra-particle diffusion. Furthermore, the Langmuir isotherm model showed a better fit with equilibrium data ($R^2 > 0.99$), with the maximum adsorption capacity of 39.47 mg·g$^{-1}$ at 25 °C. Moreover, the thermodynamic parameters indicated that the adsorption of MO onto CMC was a spontaneous and endothermic process. The results of this study indicated that CMC could be used as a promising biomass adsorbent material for aqueous solutions containing MO.

Key words | adsorption, biochar adsorbent, chicken manure, pyrolysis

INTRODUCTION
Organic dyes are well known as toxic and carcinogenic organic substances. Like many other dyes, methyl orange (MO) or acid orange 52 is widely used in textile, paper manufacturing, printing, food, and pharmaceutical industries. It can enter into the body through ingestion, and be metabolized into aromatic amines by intestinal microorganisms inadvertently (Mittal et al. 2017). Many physical and chemical methods including coagulation, flocculation, precipitation, filtration, adsorption, chemical degradation and ozonation have been used for the treatment of dye-containing effluents. Among these methods, adsorption is considered to be the most popular method due to its low cost, easy operation and high removal efficiency (Albanis et al. 2000). Because of the high sorption capacity and the specific surface area properties, activated carbon is usually used for the removal of various organic and inorganic contaminants from wastewater. However, the drawbacks of adsorption technology are difficult to regenerate after removing toxic contaminants. In view of this, the cheaper and eco-friendly biomass wastes such as agricultural waste, manure, and municipal sludge (Tan et al. 2015) have been conducted for the production of biochar adsorbents as a potential wastewater adsorption materials in wastewater treatment. Biochar adsorbents have been increasingly concerned due to their widely available biomass material, carbon-negative function, enriched surface functional groups and high-adsorption capacity. And as a relatively simple, inexpensive and robust thermochemical technology, pyrolysis is widely used for transforming biomass into biochar under oxygen limited conditions (Keiluweit et al. 2010). The chemical compositions of the insoluble chicken manure largely consist of cellulose, lignin and proteins, containing rich carbon content and oxygen containing functional groups (OFGs), such as hydroxyl, carbonyl, and carboxylic groups. Thus, chicken manure is one kind of ideal biomass feedstock for biochar preparation, and biochar adsorbent derived from chicken manure could mitigate undesirable environmental and health issues, to some extent. Although dyes in aqueous solutions have been removed by various biochars (Jin et al. 2016), detailed chemical equations are required to explain the mechanism. In addition, investigations on using biochar adsorbents derived from chicken manure for MO adsorption were not, in our knowledge, reported in the literature.

doi: 10.2166/wst.2018.003
Therefore, this study evaluated the general adsorption potential of biochar adsorbents derived from chicken manure through the MO adsorption experiments. The influences of operational parameters such as agitation speed, initial solution pH, biochar dosage and contact time on the efficiency of adsorption were investigated. The mechanism of adsorption was further determined using the adsorption kinetic models, isotherm models and thermodynamic analysis.

**MATERIALS AND METHODS**

**Adsorbate**

MO, a cationic dye, used to investigate the adsorption capability of the prepared biochar was purchased from Sigma-Aldrich without any pretreatment. A stock solution of 500 mg·L⁻¹ MO was prepared in an amber colored volumetric flask and diluted to the required concentrations (25–90 mg·L⁻¹) with deionized water.

**Preparation and characterization of biochar adsorbent**

The raw chicken manure was obtained from a local farm in the suburbs of Dalian, a city of Liaoning Province in China, and corn, wheat bran and bean pulp were provided as the diet of the chicken. The raw chicken manure was air-dried for 2 days before being oven-dried overnight at 105 °C. Then the sample was ground into particles with an average size smaller than 0.178 mm.

The preparation of carboxymethyl cellulose (CMC) was completed by a pyrolysis process. First of all, a quartz boat was filled with 10 g of chicken manure and the system ran under nitrogen gas (N₂) at 200 mL·min⁻¹. The temperature was increased steadily to 600 °C at a rate of 5 °C·min⁻¹, held at 600 °C for 120 min, and then cooled to room temperature. Subsequently, the carbonized sample was washed with deionized water and absolute ethyl alcohol to remove the residues and dried at 105 °C for 24 h.

The morphology and microstructure of the as-prepared CMC were analyzed with scanning electron microscopy (SEM, Hitachi S-4800, Japan). Fourier transform infrared spectra (FTIR) were carried out using a NEXUS670 FTIR equipped with a pressed KBr pellets in a wave number range of 400–4,000 cm⁻¹.

**Batch adsorption studies**

The agitation speed (50–250 rpm), initial pH (4.5–10.5) (which was controlled by adding 0.1 M HCl and 0.1 M NaOH), adsorbent dosage (0.2–1.4 g·L⁻¹) and contact time (0–360 min) was selected as the experimental parameters. Batch adsorption experiments were conducted in a coagulation mixing apparatus batch at 25 °C, 35 °C and 45 °C, respectively.

Adsorption kinetic experiments were carried out at an initial pH of 6.5 in a 500 mL beaker containing 200 mL MO solution with initial concentrations of 25 mg·L⁻¹, 50 mg·L⁻¹ and 75 mg·L⁻¹ and sorbent dose of 1.0 g·L⁻¹. The temperature, agitation speed and adsorption time were 25 ± 1 °C, 150 rpm and 360 min, respectively. Aliquots of solution samples were withdrawn at different time intervals.

Adsorption isotherm experiments were conducted in a 200 mL beaker with 50 mL MO solution of with initial concentrations of 40, 50, 60, 70, 80, 90 mg·L⁻¹, and the other conditions were the same as the kinetic experiment.

Adsorption thermodynamic experiments were performed at temperatures between 25 ± 1 °C and 45 ± 1 °C. MO solutions (50 mL) with an initial concentration of 50 mg·L⁻¹ were agitated with 0.05 g of sorbent dose at 150 rpm for 360 min.

The adsorbent was separated from the solution by the 0.45 μm filter membrane. The concentration of the MO dye in aqueous solution was determined by spectrometry (UV-vis spectrophotometer, 756PC Shanghai, China) at λ_max = 464 nm. All the experiments were performed in three replicates and the results were averaged with standard deviations. The removal efficiency of MO and the amount of dye adsorbed per weight of activated carbon, q(t) (mg·g⁻¹) can be calculated using the following equations:

\[
\text{Removal efficiency (\%)} = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\% \tag{1}
\]

\[
\text{Adsorption amount (mg·g}^{-1}) = \left(\frac{C_0 - C_t}{C_0}\right) \times \frac{V}{m} \tag{2}
\]

In Equations (1) and (2), \(C_0\) (mg·L⁻¹) is the initial MO concentration (mg·L⁻¹); \(C_t\) (mg·L⁻¹) is the MO concentration at time \(t\) (min); \(V\) (L) is the volume of MO solution; and \(m\) (g) is the weight of adsorbent used.

**Kinetic and isotherm models**

The mechanism of adsorption depends on the chemical reaction, diffusion control, as well as the mass transport process. The kinetic adsorption data from the adsorption of MO on CMC were simulated with four kinetic models including
pseudo-first-order (Lagrgren 1898), pseudo-second-order (Ho & McKay 1999), intra-particle diffusion (Weber & Morris 1963) and Elovich model (Chien & Clayton 1980). These formulas are given as:

\[ \log(q_e - q_t) = -\frac{k_1}{2.303} t + \log q_e \]  
(3)

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  
(4)

\[ q_t = k_{id} t^{0.5} + C \]  
(5)

\[ q_t = \frac{1}{\beta} \ln(\alpha t) + \frac{1}{\beta} \ln t \]  
(6)

where, in Equations (3)–(6), \( t \) is the contact time (min), \( q_e \) (mg·g\(^{-1}\)) and \( q_t \) (mg·g\(^{-1}\)) are the quantities of MO adsorbed onto the CMC at the equilibrium and the particular time, respectively; \( k_1 \) (min\(^{-1}\)), \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) and \( k_{id} \) (mg·g\(^{-1}\)·min\(^{1/2}\)) are the rate constant of the pseudo-first-order and pseudo-second-order and intra-particle diffusion model, respectively; \( C \) is a constant, \( \alpha \) is the initial adsorption coefficient (mg·g\(^{-1}\)·min\(^{-1}\)), and \( \beta \) is the desorption coefficient (g·mg\(^{-1}\)).

To describe the relationship between the amount of dye adsorbed and its equilibrium concentration in solution at three temperatures (25 °C, 35 °C and 45 °C), four adsorption isotherm models of Langmuir (Langmuir 1917), Freundlich (Freundlich 1906), Temkin (Temkin 1941) and Dubinin-Radushkevich (D-R) (Onyango et al. 2004) were selected to fit the adsorption isotherms. The linear form of these isotherm equations are in Equations (7)–(13).

The linear form of Langmuir isotherm equation is

\[ \frac{C_e}{q_e} = \frac{1}{Q_{\text{max}} b} + \frac{C_e}{Q_{\text{max}}} \]  
(7)

The linear form of Freundlich isotherm equation is:

\[ \ln q_e = \ln K_f + \frac{1}{n} (\ln C_e) \]  
(8)

The linear form of Temkin isotherm equation is:

\[ q_e = B(\ln A) + B(\ln C_e) \]  
(9)

\[ B = \frac{RT}{b} \]  
(10)

The linear form of D-R adsorption isotherm equations is:

\[ \ln(q_e) = \ln(q_{m1}) - \beta e^2 \]  
(11)

\[ \varepsilon = RT(1 + \frac{1}{C_e}) \]  
(12)

\[ E_a = \frac{1}{\sqrt{2\beta}} \]  
(13)

where \( C_e \) (mg·L\(^{-1}\)) is the equilibrium concentration, \( q_e \) (mg·g\(^{-1}\)) is the adsorption capacity at equilibrium time, \( Q_{\text{max}} \) (mg·g\(^{-1}\)) and \( b \) (L·mg\(^{-1}\)) are the monolayer adsorption capacity and the Langmuir rate constant, respectively, \( K_f \) (L·mg\(^{-1}\)) is the Freundlich coefficient, \( n \) is the adsorption ‘intensity’, \( A \) (L·mg\(^{-1}\)) is the equilibrium binding constant, \( b \) and \( B \) are the Temkin isotherm constants, \( R \) is the universal gas constant (8.314 J·mol\(^{-1}\)·K\(^{-1}\)), \( T \) (K) is absolute temperature, the quotient ‘\( RT/b' \) (J·mol\(^{-1}\)) is related to the heat of adsorption, \( q_{e1} \) (mol·g\(^{-1}\)) is the amount of adsorbate in the adsorbent at equilibrium, \( q_{m1} \) (mol·g\(^{-1}\)) is the theoretical isotherm saturation capacity, \( \beta \) (mol\(^{2}\)·kJ\(^{-2}\)) and \( \varepsilon \) are D-R isotherm constant and the Polanyi potential, respectively. \( E_a \) (kJ·mol\(^{-1}\)) is the free energy per molecule of adsorbate.

RESULTS AND DISCUSSION

Characterization

The morphological structure of CM and CMC were examined by SEM images, shown in Figure 1. As seen in Figure 1(a), it was demonstrated that the CM consisted of numerous rough fine particles, randomly stacking together. Upon pyrolyzation, the irregular and heterogeneous porous surface’s structure (Figure 1(b)) appeared which could be attributed to the dehydration and the oxidation of organic compounds in the carbonization step. It also suggested that a great capacity for MO adsorption was due to a great number of physical adsorption sites produced.

The FTIR spectrum of CM and CMC were shown in Figure 2. Chicken manure contained more functional groups. The peak at 3,500–3,300 cm\(^{-1}\) indicates the existence of -OH group. The bands at 2,920 cm\(^{-1}\) and 2,840 cm\(^{-1}\) can be assigned to functional groups of aliphatic C-H stretching vibration, while the peaks between 700 and 900 cm\(^{-1}\) can be assigned to aromatic C-H stretching vibration.
vibration. The bands at 1,645 cm\(^{-1}\), 1,416 cm\(^{-1}\), 1,327 cm\(^{-1}\) and 1,058 cm\(^{-1}\) are assigned to C=O of carboxylic acids, -CH\(_2\) of alkanes, C-N of aromatic amines and C-O of carboxylates, respectively. The peak at 467 cm\(^{-1}\) is attributed to Si-O-Si. After pyrolysis process, the disappearance of some distinctive peaks such as C-H, C=O and C-O vibration, indicated that hydrogen and oxygen were broadly removed during carbonization process (Mahamad et al. 2015).

**Effect of agitation speed**

The effect of agitation speed was evaluated under the following conditions: initial dye concentration of 25 mg L\(^{-1}\), temperature of 25 ± 1 °C, 0.05 g of adsorbent and volume of solution 50 mL. The pH and adsorption time were 6.5 and 120 min, respectively. The results are shown in Figure 3(a). As the agitation speed was increased from 50 rpm to 250 rpm, the removal efficiency of MO increased. This could be explained that the higher agitation speed leaded to an increase of liquid shearing action in solution, and then the liquid film mass transfer rate was increased between MO and CMC, which resulted in high adsorption of MO. Furthermore, with the increase of agitation speed, the opportunity of touch between MO molecules and adsorbent microparticles was increased, which was due to the increased unstable dispersion degree of CMC in solution. The above two factors promoted the CMC for MO adsorption. Compared with the agitation speed of 150 rpm, the speed of 200 rpm or 250 rpm had no significant increase of the removal efficiency of MO. The higher agitation speed would consume more energy, thus, 150 rpm was chosen as the optimum agitation speed for the following batch experiments.

**Effect of initial pH**

The effect of pH was evaluated under the following conditions: initial dye concentration of 25 mg L\(^{-1}\), temperature of 25 ± 1 °C, 0.05 g of adsorbent and volume of solution 50 mL. The agitation speed and adsorption time were 150 rpm and 30 min, respectively. The results are shown in Figure 3(b). The adsorption efficiency and \(q_t\) decreased from 89.19% and 22.30 mg g\(^{-1}\) to 81.67% and 20.42 mg g\(^{-1}\), respectively. When the pH was changed from 4.5 to 10.5, it could be seen that the \(q_t\) obviously decreased. These results could be explained that the surface charge of CMC changed with different pH. As the pH value in acidic condition
(4.5–6.5), and the protonation of functional groups such as -OH₂⁺ and -NH₃⁺ in CMC made them more available to adsorb anionic MO through electrostatic attraction (Chen et al. 2011). As the initial pH increased from 7.5 to 10.5, the competition between OH⁻ and anionic MO for positively charged adsorption sites caused a decline of MO adsorption. To increase the adsorption capacity and keep natural pH value of MO dye solutions, the initial pH of 6.5 was selected for the rest of the batch experiments.

**Effect of adsorbent dosage**

The effect of adsorbent dosage was evaluated under the following conditions: initial dye concentration of 25 mg·L⁻¹, pH of 6.5, and temperature of 25 ± 1 °C. The agitation speed and adsorption time were 150 rpm and 30 min, respectively. The results are shown in Figure 3(c). The effect on the removal of MO was illustrated in Figure 5. The increase in CMC dosage from 0.2 g·L⁻¹ to 1.4 g·L⁻¹ caused the increase in MO adsorption efficiency from 29.37% to 100%. The results indicated that the removal of MO was gradually increased with the dosage to reach almost 100% when the dosage of 1.0 g·L⁻¹ was employed. The increase in MO adsorption with the adsorbent dosage was attributed to the increase of the surface area on CMC, which could provide more vacant adsorption sites. The constant removal efficiency of MO was observed when the dosage was more than 1.0 g·L⁻¹, and it was probably due to the occurrence of great surface area and an increase in the number of binding sites (Jain et al. 2010). However, the qₑ values for all adsorbents were decreased from 36.72 mg·g⁻¹ to 17.86 mg·g⁻¹ with increasing adsorbent dosage due to competition or overlapping between the MO dye molecules, which were bound to the available adsorption sites of the adsorbent (Wang et al. 2010). Consequently, the optimal adsorbent dosage was chosen as 1.0 g·L⁻¹ for the following batch experiments.
Effect of contact time

The effect of contact time at different initial solution concentrations (25, 50 and 75 mg·L⁻¹) was evaluated under the following conditions: initial pH of 6.5, temperature of 25 ± 1 °C, 0.05 g of adsorbent and volume of solution 50 mL. The agitation speed and adsorption time were 150 rpm and 360 min, respectively. The results are shown in Figure 3(d). It was seen that the whole process was evidently divided into three sections at different initial solution concentrations: (1) an initial rapid stage where the adsorption rate was fast (0–30 min), (2) a slower second stage where the adsorption rate became lower (30–180 min), and (3) the lowest equilibrium adsorption stage (after 180 min).

At the beginning of adsorption, the driving force of the concentration gradient between CMC and MO solution was larger, and the adsorption rate was relatively rapid. The value of \( q_t \) was increased significantly with the time, which might be related to the high vacant active sites of the adsorbent surface. After this stage, the driving force of the concentration gradient and surface active sites became small and decreasing, respectively, and then, the remaining vacant surface sites were different to occupy because of the repulsive forces between the MO dye molecules on the CMC and the bulk phase, the value of \( q_t \) was increased in small range. Eventually, it reached adsorption equilibrium at 180 min of the contact time in all curves. Moreover, the equilibrium capacities were 24.98, 35.04 and 38.35 mg·g⁻¹ for the 25, 50 and 75 mg·L⁻¹ MO solution, which were also confirmed by other investigators (Deng et al. 2009; Gulnaz et al. 2004) and they attributed this phenomenon to the increase in the driving force of the concentration gradient, with the increase of the initial dye concentration. Hence a higher initial concentration of MO dye would enhance the adsorption capacity of CMC in this study. However, the maximum adsorption capacity was reported to be 16.30 mg·g⁻¹ for pig manure derived biochar adsorbent at methylene blue concentration of 50 mg·L⁻¹ (Linson et al. 2016).

Adsorption kinetics

The adsorption kinetics and parameters give important information for designing and modeling the adsorption processes. Figure 4 and Table 1 showed the adsorption kinetic curves and fitting parameters of MO solution onto CMC with the different initial MO concentrations at 25 ± 1 °C. It was found that the \( R^2 \) values for the pseudo-second-order model were close to 1.0 and the \( q_e \) values were also very close to those experimental values (24.98, 35.04 and 38.35 mg·g⁻¹) at the different initial concentrations, respectively. These results indicated that the adsorption of MO dye onto the CMC followed the pseudo-second-order model. However, the rate constant \( k_2 \) decreased with increasing the initial MO concentration because the mass transfer did not occur well at lower MO concentration. The intra-particle diffusion model might present multi-linearity, indicating that two stages took place. The first stage was related to the mass transfer of MO to the surface of the CMC while the second stage was assigned for intra-particle diffusion of MO into the CMC. The \( k_{id1} \) (0.959–2.051) and \( k_{id2} \) (0.0075–0.133) indicated that the fast MO mass transfer to the surface of the CMC occurred at the initial stage and was followed by slow MO intra-particle diffusion into internal pores of the CMC. The correlation coefficients \( R^2 \) of the pseudo-first-order and Elovich were low without a definite role.

Adsorption isotherm

The equilibrium adsorption test provides the physicochemical data on the applicability of the adsorption. The fitting results were presented in Figure 5 and Table 2. It was obvious that the experimental results were well represented by the Langmuir and Freundlich isotherms with a correlation coefficients \( R^2 \) higher than 0.99 and 0.97, respectively. It was demonstrated that the MO molecules formed monolayer coverage on the prepared CMC, which was homogenous in nature under the condition in this study. This also suggested that every adsorption site of CMC had the same adsorption energy and the \( b \) values were 0.726, 0.778 and 0.806 mg·L⁻¹ with the increase of temperature, respectively. Moreover, the values of the Freundlich exponent \((1/n) < 1\) indicated that the systems were favorable and easy.

The Temkin isotherm model mainly describes the chemical adsorption process as electrostatic interaction (Leng et al. 2015). In the present study, the Temkin isotherm fitted the observed results well \((R^2 > 0.96)\). Therefore, electrostatic interaction was also an important mechanism affecting the interaction between CMC and MO. However, the low correlation coefficients \( R^2 < 0.87 \) indicated that D-R isotherm did not describe the adsorption of MO onto CMC well. In addition, it could be seen that the maximum adsorption capacity was increased from 39.37 to 41.49 mg·g⁻¹, with the temperature increasing from 25 °C to 45 °C, which indicated that raising the operational
temperature could enhance the adsorption behavior. This phenomenon would be further discussed in the section of adsorption thermodynamics.

**Adsorption thermodynamics**

To further understand the adsorption process between MO and CMC, thermodynamic parameters were determined at three different temperatures (25 °C, 35 °C, and 45 °C). The ΔG° (kJ·mol⁻¹) could be calculated by the following equation (Saucier *et al.* 2015):

\[
\Delta G^0 = -RT\ln K^0
\]

(14)

The Van’t Hoff equation was used to calculate the values of ΔH° (kJ·mol⁻¹) and ΔS° (J·(mol·K)⁻¹). After substituting of \( \Delta G^0 = \Delta H^0 - T\Delta S^0 \) into Equation (14), it could be rewritten as follows:

\[
\ln K^0 = -\frac{\Delta G^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(15)

R (8.314 J·mol⁻¹·K⁻¹), T (K) and \( K_0 \) in the equation represented the universal gas constant, the absolute temperature and the equilibrium constant equals to \( q_e/C_e \), respectively. \( \Delta H^0 \) and \( \Delta S^0 \) could be calculated from the slope and intercept of Equation (15), respectively. The obtained thermodynamic parameters values including \( \ln K^0, \Delta G^0, \Delta H^0 \) and \( \Delta S^0 \) were given at various temperatures in Table 3. These negative values of \( \Delta G^0 \) demonstrated that the adsorption of MO on the CMC was a feasible and spontaneous process. The absolute value of \( \Delta G^0 \) was increased with the enhancement of adsorption temperature, revealing that the increasing adsorption temperature was in favor of adsorption. Positive values of \( \Delta H^0 \) were obtained, proposing
Figure 5 | Isotherm fits for MO adsorption on CMC using different models: (a) Langmuir; (b) Freundlich; (c) Temkin; and (d) Dubinin–Radushkevich.

Table 1 | Kinetic parameters of MO onto CMC for various isotherm models (pseudo-first-order, pseudo-second-order, intra-particle diffusion and Elovich models)

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Kinetic parameters</th>
<th>25</th>
<th>50</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>(k_1)</td>
<td>0.02867</td>
<td>0.00229</td>
<td>0.00084</td>
</tr>
<tr>
<td></td>
<td>(q_e)</td>
<td>2.10</td>
<td>21.43</td>
<td>43.85</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.902</td>
<td>0.428</td>
<td>0.392</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>(k_2)</td>
<td>0.0404</td>
<td>0.0107</td>
<td>0.0093</td>
</tr>
<tr>
<td></td>
<td>(q_e)</td>
<td>25.16</td>
<td>35.46</td>
<td>38.61</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.999</td>
<td>0.999</td>
<td>0.999</td>
</tr>
<tr>
<td>Intra-particle diffusion</td>
<td>(k_{ad1})</td>
<td>0.959</td>
<td>1.847</td>
<td>2.051</td>
</tr>
<tr>
<td></td>
<td>(k_{ad2})</td>
<td>0.0075</td>
<td>0.133</td>
<td>0.116</td>
</tr>
<tr>
<td></td>
<td>(C_1)</td>
<td>18.31</td>
<td>20.48</td>
<td>22.34</td>
</tr>
<tr>
<td></td>
<td>(C_2)</td>
<td>24.86</td>
<td>32.98</td>
<td>36.41</td>
</tr>
<tr>
<td></td>
<td>(R_1^2)</td>
<td>0.903</td>
<td>0.940</td>
<td>0.937</td>
</tr>
<tr>
<td></td>
<td>(R_2^2)</td>
<td>0.911</td>
<td>0.813</td>
<td>0.776</td>
</tr>
<tr>
<td>Elovich</td>
<td>(\alpha)</td>
<td>3.05 \times 10^6</td>
<td>4.08 \times 10^3</td>
<td>4.48 \times 10^3</td>
</tr>
<tr>
<td></td>
<td>(\beta)</td>
<td>0.778</td>
<td>0.352</td>
<td>0.322</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.922</td>
<td>0.925</td>
<td>0.919</td>
</tr>
</tbody>
</table>

Table 2 | Isotherm parameters of MO onto CMC for various isotherm models (Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models)

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Isotherm parameters</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>Langmuir</td>
<td>(b)</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td>(Q_{\text{max}})</td>
<td>39.37</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich</td>
<td>(k_f)</td>
<td>29.70</td>
</tr>
<tr>
<td></td>
<td>(1/n)</td>
<td>0.0675</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.975</td>
</tr>
<tr>
<td>Temkin</td>
<td>(A)</td>
<td>1.64 \times 10^5</td>
</tr>
<tr>
<td></td>
<td>(B)</td>
<td>2.427</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.982</td>
</tr>
<tr>
<td>D-R</td>
<td>(\beta)</td>
<td>10.6 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>(E_a)</td>
<td>22.27</td>
</tr>
<tr>
<td></td>
<td>(R^2)</td>
<td>0.879</td>
</tr>
</tbody>
</table>
that the adsorption of MO on the CMC was an endothermic process (Ding et al. 2014), and the positive values of $\Delta S^0$ indicated an increase in the degree of disorder and randomness at solid/solution interface during the adsorption of MO onto CMC (Khan et al. 2013).

**CONCLUSIONS**

It was evident that biochar adsorbent derived from chicken manure was an effective sorbent for MO anionic dye. The physicochemical properties of CMC before and after pyrolysis were synthesized and fully characterized using SEM and FTIR. The adsorption process was systematically studied and researched under different conditions including agitation speed, initial solution pH, biochar dosage and contact time. The equilibrium for the adsorbate was obtained after a contact time of 60 min. The acidic pH had a more significant effect on the adsorption of MO than the neutral and alkaline pH. The adsorption kinetic curves and fitting parameters showed that the adsorption rate could be considered to be a pseudo-second-order model. Results obtained from this study were well described by Langmuir, Freundlich and Temkin isotherm models and a lower degree by Dubinin–Radushkevich isotherm model. The adsorption of MO onto CMC was found to be spontaneous and endothermic in nature and the decrease of $\Delta G^0$ values implied that higher temperature favored the MO adsorption. The mechanism for the adsorption of MO onto the CMC might include pore filling and electrostatic interaction. These results suggested that CMC could be employed as a promising and valuable absorbent to remove MO from wastewater.

**ACKNOWLEDGEMENTS**

This work was supported by a crossing research project of School of Environmental Science & Technology, Dalian University of Technology (HX20160605).

**REFERENCES**


**Table 3** | Thermodynamic parameters of MO adsorption on CMC at various temperatures

<table>
<thead>
<tr>
<th>Thermodynamic parameter</th>
<th>Temperature (°C)</th>
<th>25</th>
<th>35</th>
<th>45</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>InK°</strong></td>
<td></td>
<td>0.904</td>
<td>1.029</td>
<td>1.095</td>
</tr>
<tr>
<td><strong>ΔG°</strong></td>
<td></td>
<td>−2.240</td>
<td>−2.636</td>
<td>−2.896</td>
</tr>
<tr>
<td><strong>ΔH°</strong></td>
<td></td>
<td>7.558</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>ΔS°</strong></td>
<td></td>
<td>32.948</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
methylene blue on biochar microparticles derived from different waste materials. Waste Management 49, 537–544.

First received 3 June 2017; accepted in revised form 21 December 2017. Available online 4 January 2018