Modification of waste coal gangue and its application in the removal of Mn$^{2+}$ from aqueous solution
Ruifang Qiu and Fangqin Cheng

ABSTRACT
We developed a new calcination method to convert coal gangue (CG), a common waste generated from coal production process, into a modified form, which could be used as an adsorbent to remove Mn$^{2+}$ from aqueous solution. Sodium tetraborate (Na$_2$B$_4$O$_7$·10H$_2$O) was added into the CG calcination process as an additive, and the concentrations of Na$_2$B$_4$O$_7$·10H$_2$O were optimized along with the calcination temperature to obtain the best adsorbent capacity of modified coal gangue (MCG). We applied multiple analytical methods such as scanning electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy and Brunauer–Emmett–Teller analysis to characterize the MCG. The results showed it had a smaller particle size and a larger specific surface area and pore volume after modification. It also indicated that the phase of CG transformed from kaolinite to metakaolinite after calcination. Moreover, a new substance was generated with two new peaks at 1,632 cm$^{-1}$ and 799 cm$^{-1}$. The Mn$^{2+}$ absorption capacity of MCG was evaluated using a series of experiments with different adsorbent doses, pH values and initial Mn$^{2+}$ concentrations during the adsorption process. We found that Mn$^{2+}$ adsorbent capacity of MCG increased by more than seven-fold compared to that of CG. The Langmuir isotherm model and the pseudo-second-order kinetic model provided the best fit to the adsorption processes.

Key words | adsorption, calcination, coal gangue, manganese (Mn$^{2+}$), sodium tetraborate

INTRODUCTION
Coal gangue (CG) is the remaining stone after ore mineral has been excavated and coal has been washed. The average generation of CG is 10%–15% of total amount of raw coal production in China. The vast amount of CG is usually piled in the open air. This is not only causing local ecological and environmental hazards, but also threatening the safety of local residents. Therefore, many attempts have been made to utilize CG in an eco-friendly way. Also, as a low efficacy fuel in power generation, CG was often used as the raw material to produce zeolites and as a replacement of clay in building construction, because CG has high content of clay minerals and aluminosilicate (Li et al. 2006a, 2006b; Zhang et al. 2011). On the other hand, many studies have shown that clay minerals are promising adsorbents to remove heavy metal pollutants from water, and the adsorption capacity could be optimized through intercalation, pillarization, and chemical and thermal treatments (Unuabonah et al. 2008; Akar et al. 2009; Ghorbel-Abid et al. 2010). However, there is no study to test the possibility of CG being a potential raw material to develop adsorbents because of its high content of clay minerals. The modification of the microscopic structure of CG through a well-designed calcination method could make CG a low-cost adsorbent to remove heavy metal pollutants from industrial wastewater.

Manganese (Mn) is a heavy metal element having many applications in industry, for example, metallurgical processes, chemical manufacturing, dry-cell battery making, leather and textile manufacturing, and drugs and supplements production. Although manganese is an essential mineral for humans, the excessive exposure to manganese poses risks to human health, such as adverse effects on the nervous system, inflammatory responses of lung, and impaired sexual functions (Reaney et al. 2002). Manganese causes different degrees of toxicity depending on its particular oxidation states. The manganese oxide with low valence states has much stronger toxicity than that of high valence states (Reaney et al. 2002).

Manganese removal from aqueous solution and industrial effluent has been studied previously. Conventional treatment for the Mn(II) removal generally required strong oxidizing agents such as potassium permanganate, chlorine,
hypochlorite, chlorine dioxide or ozone (Bhattacharyya & Gupta 2008), but it would potentially generate new pollutants and toxins. Currently, membrane filtration, chemical precipitation and ion exchange are among the most commonly used methods for the heavy metal removal treatment. However, many of them are too expensive and relatively less effective (Tran et al. 1999; Olu-Owolabi & Unuabonah 2011). Compared to previous approaches, adsorption has been considered as the most preferred method to remove heavy metals from the wastewater, especially in the developing countries. It has several advantages: efficacy at very low concentrations of heavy metals, applicability in batch and continuous industrial processes, simplicity of operation, low generation of sludge, high possibility of adsorbent regeneration and reuse, and less operating cost (Unuabonah et al. 2008; Akar et al. 2009; Ghorbel-Abid et al. 2010). A few studies proposed using synthesized materials such as mesoporous silica and active carbon to be the adsorbents to remove Mn2+ residues in aqueous solution, but the costs are still high in the developing countries (Silvio & Jorge 2013; Akpo-mie & Dawodu 2014; Idris 2015). Thus, there is a need to develop low-cost adsorbents, for example, modified coal gangue (MCG), to remove Mn2+ in wastewater.

Therefore, the objectives of this work were: (1) to optimize calcination conditions of the CG, for example, the concentration of additive sodium tetraborate (Na2B4O7·10H2O) and the calcination temperature, to generate MCG which has the best adsorbent capacity for Mn2+; (2) to systematically characterize the MCG by using scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TG) and point of zero charge (PZC) experiments; (3) to evaluate the effect of system parameters (initial Mn2+ concentration, adsorbent dose, solution pH, adsorption kinetics and isotherms) and investigate the mechanisms of the adsorption behavior.

MATERIALS AND METHODS

Materials

CG sample used in this study was collected from Pingshuo coal mine, Shanxi province, China. It was crushed, ground and screened to a particle size <120 μm and stored in closed containers for further treatment. The chemical composition of CG was determined by energy dispersive X-ray fluorescence (Bruker S8 TIGER, Germany) as shown in Table 1.

**Preparation of modified adsorbent and solution**

CG (10 g) with a certain concentration of additive Na2B4O7·10H2O was heated in a muffle oven for 2 h with a heating rate of 20 °C min⁻¹. The mixture was then placed in a stove at 100 °C and afterward in a desiccator until it reached ambient temperature (25 °C). Then it was sieved to <120 μm particle size before use as adsorbent. The sample was marked MCG. To quantitatively evaluate the relationship between calcination temperature and Mn2+ adsorption performance, the mixture was calcinated at different temperature of 400, 500, 600, 700, 800, 900 and 1,000 °C. In addition, to detect the effect of Na2B4O7·10H2O on Mn2+ removal performance, varying, Na2B4O7·10H2O percentages (m/m) corresponding to 3, 5, 8 and 10% were used.

Simulated stock wastewaters with 1,000 mg L⁻¹ Mn2+ were prepared by dissolving appropriate amounts of MnSO4·7H2O in Milli-Q water. The desired concentrations in experiments were prepared by diluting stock wastewater. The pH was adjusted using 0.1 mol L⁻¹ HCl or 0.1 mol L⁻¹ NaOH solution. All chemicals used in this study were analytical reagent grade. Milli-Q water was used in all experiments.

**Characterization**

TG of the samples was carried out by a thermogravimeter (Perkin-Elmer Pyris1, USA) in a flowing air atmosphere with a heating rate of 20 °C min⁻¹. The morphology of the samples was analyzed by SEM (JSM7001F, Japan). The mineral composition of the samples was determined by XRD (Bruker D2-Phaser, Germany) using CuKα1 radiation. The pattern was recorded per a 2θ interval of 10° to 90°, with a scanning speed of 0.6 °minute⁻¹. The infrared spectroscopy with Fourier transformation (Perkin Elmer Frontier, USA) was carried out using pellets of KBr in the range 4,000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹. The

### Table 1 | Chemical composition of CG

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>MgO</th>
<th>P₂O₅</th>
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<tbody>
<tr>
<td>Contents (%)</td>
<td>55.37</td>
<td>31.62</td>
<td>3.89</td>
<td>3.79</td>
<td>2.15</td>
<td>1.28</td>
<td>0.72</td>
<td>0.51</td>
<td>0.14</td>
</tr>
</tbody>
</table>
Brunauer–Emmett–Teller (BET) surface area of the samples was determined using a BET-N₂ area analyzer (Micromeritics ASAP2020, America). The zeta potential of the samples was measured using a zeta potential analyzer (Malvern Nano ZS90, UK). Twenty measurements were carried out to arrive at a representative average measured potential. The concentration of Mn²⁺ was determined using an atomic absorption spectrophotometer (Shimadzu AA-6700, Japan).

**Mn²⁺ adsorption experiments**

The adsorption experiments of Mn²⁺ by MCG and CG were carried out according to batch method. A series of 100 mL conical flasks were filled with 25 mL of Mn²⁺ solutions, and a known amount of adsorbent dosage was then added to each conical flask. The flasks were shaken for the desired contact time in a shaker incubator at 150 rpm. To study the effect of adsorbent dose, 0.125, 0.250, 0.375 and 0.500 g of adsorbent, respectively, were placed in contact with Mn²⁺ solution of an initial concentration of 100 mg L⁻¹ for 2 h. The effects of initial solution pH on the adsorption of Mn²⁺ was conducted by the batch adsorption process described above adjusting initial pH to 1.0 to 7.0 by 0.1 mol L⁻¹ HCl solution or 0.1 mol L⁻¹ NaOH solution under the following conditions: adsorbent dosage of 0.250 g; initial Mn²⁺ concentration of 100 mg L⁻¹; contact time of 2 h. To verify the effect of the initial concentration, solutions at concentrations corresponding to 25, 50, 100, 200 and 300 mg L⁻¹ were used. The adsorption equilibrium experiments were under the following conditions: adsorbent dosage of 0.125 g; initial pH of 6.0; contact time of 2 h. The adsorption kinetics study was carried out at preset intervals of time (10–180 min) under the conditions as above. All experiments were carried out in duplicate and the data were presented with the average value, to confirm the reproducibility of the results.

**RESULTS AND DISCUSSION**

**Modification of CG**

**Effect of calcination temperature**

As shown in Figure 1, Mn²⁺ adsorption was found to decrease both at the lower and higher calcination temperature with somewhat higher adsorption at 500 °C. The changes in CG calcination progress as a function of temperature are measured by thermal analysis. Figure 2 shows the derivative of the weight loss (differential thermal gravity (DTG)) and TG curves with the calcination temperature of CG and MCG under air atmosphere. According to the TG curve, the weight loss of CG and MCG both reached up to about 30% and stabilized at 700 °C. In the temperature interval between 50 and 300 °C, the loss of mass was approximately 6%, which was probably due to the loss of surface water, void water, bound water and impurities that were retained on the surface of CG and MCG. And then, the weight loss at 300–700 °C was attributed to the high temperature thermal decomposition of some organic matter and dehydroxylation of kaolinite (Ptácek et al. 2014). But the loss of MCG is higher than CG before 550 °C. It is because Na₂B₄O₇·10H₂O in MCG loses the crystal water at about 380 °C and dehydration process is finished before 550 °C (Aysu & Durak 2015). It was in accordance with DTG analysis showing three peaks for MCG and one peak for CG. From the results obtained, Na₂B₄O₇·10H₂O as an additive may promote the dehydration
process of CG, and borate weakened and broke the bonds of CG to form new networks of silicates and borates as well as other oxide phases (Zhang et al. 2011), which contribute to a loose and porous structure and increase pore volume and specific surface area as shown in Table 2. However, Mn\(^{2+}\) adsorption decreased gradually with the increasing of temperature; it could be explained by the recrystallization of kaolinite and other minerals such as mullite and illite (Zhou et al. 2012). On the other hand, the fusion of Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O at 878 °C leads to presence of glass state including B\(_2\)O\(_3\) that can be reacted with metallic oxide. So these recrystallization and fusion processes have a negative impact on porous structure and specific surface area.

### Effect of Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O percentage

As shown in Figure 3, when percentages of Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O increased from 3% to 8%, Mn\(^{2+}\) adsorbed on MCG increased from 4.92 to 7.91 mg g\(^{-1}\). However, when Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O further increased to 10%, the amount of Mn\(^{2+}\) adsorbed on MCG increased slightly to 7.98 mg g\(^{-1}\). Compared to only 1.04 mg g\(^{-1}\) adsorbed on CG, it suggested that the adsorption capability can be improved markedly using CG modified by calcination with Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O as an additive. As shown in Table 2, the specific surface area increased from 9.29 m\(^2\) g\(^{-1}\) to 20.05 m\(^2\) g\(^{-1}\) after modification. The result shows that the calcination modification with Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O increased specific surface area significantly. Hence, the optimal calcination temperature and amount of Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O were 8% and 500 °C, respectively.

### Characterization

#### SEM and XRD analysis

SEM was used to check the solid morphology and average crystal size of the CG and MCG adsorbents. As shown in Figure 4, the surface of MCG granules had a flaky appearance. The size of MCG is obviously smaller than CG. The mean particle diameter of MCG and CG is 9.05 μm and 112.38 μm, respectively (Figure 5). Furthermore, the pore volume increased to 0.097 cm\(^3\) g\(^{-1}\) from 0.015 cm\(^3\) g\(^{-1}\) after modification. The minerals such as kaolinite and organic matter, especially carbon, may have significantly contributed to the transformation of the CG morphological characteristic during calcination. The original structure could be broken, leading to more micro-sized particles and bigger specific surface area (Cristóbal et al. 2009). Furthermore, calcination with Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O could have weakened and broken the bonds of CG to bring about the separation of the constituent layers of CG, so guaranteeing greater accessibility for the molecules of adsorbate (De Sales et al. 2013).

The XRD patterns of CG and MCG are given in Figure 6. The main mineral phases of CG were kaolinite, quartz, illite and calcite. The peak intensities of kaolinite almost disappeared in MCG. Thus, it could be assumed that the phase transformed from kaolinite to metakaolinite after modification, which was in line with the result of thermal analysis. In addition, the peak intensities of quartz increased slightly, which could be attributed to the generation of unshaped SiO\(_2\) by the decomposition of clay minerals such as kaolinite (Jake et al. 1998). The destruction of Si-O-Al could improve the activity of MCG, which could be conducive to adsorption capacity.

#### FTIR analysis

The infrared spectrum provides important information on molecular structure, especially for the functionalities of organic compounds. The infrared spectra of CG and MCG are shown in Figure 7. In natural CG, the absorption peak at 3,698, 3,650, 1,097, 1,034, 1,010, 912, 799, 687, 533, 466 and 420 cm\(^{-1}\) could indicate the existence of kaolinite (Jake et al. 1998; Cristóbal et al. 2009; De Sales et al. 2013). The bands at 3,698 and 912 cm\(^{-1}\) represent the inner surface –OH stretching vibration and Al-O-H
bending vibration, respectively. The bands at 1,034 cm\(^{-1}\) represent Si-O stretching vibration (MacPhee et al. 2006). The bands at 3,650 and 533 cm\(^{-1}\) are due to stretching vibration of OH groups and Al-O-Si stretching vibration.

The band at 1,620 cm\(^{-1}\) resulted from the H-O-H bending vibration of H\(_2\)O (Gladysz-Plaska et al. 2012). Two split bands at 2,918 and 2,848 cm\(^{-1}\) are attributed to aliphatic C-H stretching vibration (Jin et al. 2014). The absorption
peak at 1,438 cm\(^{-1}\) belonged to CO\(_3\)\(^{2-}\) stretching vibration; it was an indication of the existence of carbonate (Cristóbal et al. 2013; De Sales et al. 2013). In addition, the absorption peak at 1,034, 1,010, 912, 799 and 466 cm\(^{-1}\) could indicate the existence of quartz (Orrego-Ruiz et al. 2014). The Si-O-Si stretching vibrational frequency at 1,034 cm\(^{-1}\), in company with the Si-O-Si bending vibrational frequencies at 799, 742 and 466 cm\(^{-1}\), was identical to the characteristic absorption peaks of illite (Jake et al. 1998); the results were consistent with the result of XRD.

Compared to CG, the absorption peaks at 3,698, 3,650, 1,034, 1,010, 912, 533 and 466 cm\(^{-1}\) decreased gradually; it was an indication that the dehydration reaction of kaolinite and illite was going on, but this had no influence on the locations of the characteristic peaks. Conversely, the absorption peak at 1,097 and 466 cm\(^{-1}\) became wider, suggesting kaolinite was made into a high-activity metakaolinite when it was dehydrated. Also, the absorption peaks at 1,632 and 799 cm\(^{-1}\) became sharp, indicating the generation of new substances.

**PZC**

As shown in Figure 8, the zeta potential of CG and MCG showed the same tendency, with a reversal of charge from positive to negative, with the increase in pH. In an acid medium, the positive surface charge may be associated with the adsorption of H\(^+\) ions in centers of negative charge, whilst in a basic medium, increase in negative charge of the adsorbent surface is due to the process of adsorption of hydroxyl ions at centers of positive charge or to the mechanism of deprotonation of hydroxyl groups present at the surface (Alkan et al. 2008). It can be seen that the modification caused decrease of the isoelectric point, which may be attributed to the change in chemical composition resulting from the treatments.

**Mn\(^{2+}\) adsorption**

**Effect of adsorbent dose**

Figure 9 shows that adsorption capacity of Mn\(^{2+}\) rapidly decreased with increasing amount of adsorbent ranging from 0.125 g to 0.250 g and then decreased more slowly as adsorbent increased to 0.500 g, although there was an obvious increase of the percentage of Mn\(^{2+}\) removal with adsorbent dose increasing. This was expected given that an increased adsorbent dose provides a larger number of available adsorption sites, thus increasing percentage of Mn\(^{2+}\) removal. However, in this case the adsorption process may be governed principally by the capacity of the molecules of adsorbate to migrate sufficiently toward the surface.
Therefore, 0.125 g (the 1:200 ratios) was defined as the most appropriate adsorbent dose for CG and MCG.

**Effect of pH**

The aqueous solution pH is an important operational parameter in the adsorption process because of its effect on the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. The effect of pH on Mn$^{2+}$ removal was investigated in the pH range 2–7 at 25°C as shown in Figure 10. With the pH increase, the adsorption capacity of MCG increased slowly, and its highest adsorption of Mn$^{2+}$ was 14.8 mg g$^{-1}$ obtained at final pH > 6.3. But it was different for CG: the adsorption was found to increase slowly (from 0.9 mg g$^{-1}$ to 1.4 mg g$^{-1}$) when pH < 3. Thereafter, the solution pH remarkably impacted on the adsorption of Mn$^{2+}$; when the solution pH increased from 3.0 to 6.3 the adsorption of Mn$^{2+}$ increased from 1.4 to 3.3 mg g$^{-1}$. The pH affects the adsorption process, which can be explained using the theory of PZC. When the pH > pH$_{PZC}$, the adsorbent surface becomes deprotonated and adsorption of cation is favored. But at pH < pH$_{PZC}$, the surface is protonated and becomes positively charged, which prevents electrostatic binding of the positively charged Mn$^{2+}$. In this case, the adsorption capacity is attributed to the porous adsorbent surface (Alkan et al. 2008). In addition, competition between Mn$^{2+}$ and H$_3$O$^+$ ions for adsorption sites on CG or MCG surface is also important (Gupta & Bhattacharyya 2008). At low pH, the number of H$_3$O$^+$ ions exceeds that of the Mn$^{2+}$ several times and the surface is most likely covered with H$_3$O$^+$ ions, which account for less Mn$^{2+}$ adsorbed. When pH increases, more and more H$_3$O$^+$ ions leave the adsorbent surface making the sites available to the Mn$^{2+}$, which now increasingly bind to adsorbent surface through a mechanism similar to that of exchange interactions (H$^+$/Mn$^{2+}$). As the pH approached a certain value, precipitation of the insoluble metal-hydroxides may appear as apparently higher metal ion removal.

**Effect of initial Mn$^{2+}$ concentration and adsorption isotherm**

There was a clear increase in the adsorption capacity of the adsorbent with increasing initial Mn$^{2+}$ concentration (Figure 11(a)). In this case, the increase in initial Mn$^{2+}$ concentration provides an important increase in driving force that overcomes the mass transfer resistance of Mn$^{2+}$ between the aqueous and solid phases. But a further increase of initial Mn$^{2+}$ concentration did not affect the adsorption significantly. The maximal adsorptive capacity of Mn$^{2+}$ on MCG and CG was 24.4 mg g$^{-1}$ and 3.4 mg g$^{-1}$, respectively. Thus, the adsorptive capacity for Mn$^{2+}$ of MCG increased over seven times compared to CG. Claudia and colleagues obtained hydrothermal synthetic zeolite from fly ash to treat Mn$^{2+}$; the removal efficiency and adsorptive capacity of Mn$^{2+}$ were 99% and 0.1 mg g$^{-1}$, respectively (Claudia et al. 2015). Activated Chilean zeolites were used to remove Mn$^{2+}$ and the adsorptive capacity was 14.3 mg g$^{-1}$ (Silvio & Jorge 2009). Akpomie and Dawodu reported the adsorptive capacity of Mn$^{2+}$ by alkaline-modified montmorillonite was 32.35 mg g$^{-1}$ (Akpomie & Dawodu 2014). Compared to these references, MCG is ideal for low-cost wastewater treatment which can improve reuse of resources to protect the environment.
Adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of a solute on an adsorbent. Adsorption isotherms can be generated based on numerous theoretical models and the Langmuir and Freundlich models are extensively used (Jin et al. 2014).

The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The model takes the following form as Equations (1) and (2):

\[
Q = \frac{Q_m k_l C_e}{1 + k_l C_e} \quad \text{(non-linear form)} \tag{1}
\]

\[
\frac{C_e}{Q} = \frac{1}{Q_m k_l} + \frac{C_e}{Q_m} \quad \text{(linear form)} \tag{2}
\]

where \(Q\) is the amount of solute adsorbed per unit weight of adsorbent (mg g\(^{-1}\)), \(C_e\) is the equilibrium concentration of solute in the bulk solution (mg L\(^{-1}\)), \(Q_m\) is the monolayer adsorption capacity (mg g\(^{-1}\)) and \(k_l\) is the constant related to the energy of adsorption (L g\(^{-1}\)).

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface. It says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich equation is commonly represented by Equations (3) and (4):

\[
Q = k_f C_e^1 \quad \text{(non-linear form)} \tag{3}
\]

\[
\log Q = \log k_f + \frac{1}{n} \log C_e \quad \text{(linear form)} \tag{4}
\]

where \(k_f\) is the constant indicative of the relative adsorption capacity of the adsorbent (mg g\(^{-1}\)) and \(n\) is the constant indicative of the intensity of the adsorption.

Table 3 and Figure 11(b) show the parameters for the Langmuir isotherm and Freundlich isotherm. The correlation coefficients (R\(^2\)) of Langmuir equations for adsorbents were all much higher than corresponding R\(^2\) of Freundlich equations, respectively. Furthermore, fitted equilibrium adsorption capacity (\(Q_m\)CG = 3.2 mg g\(^{-1}\), \(Q_m\)MCG = 23.9 mg g\(^{-1}\)) was found to be in close agreement with those tested experimentally (\(Q_m\)CG = 3.4 mg g\(^{-1}\), \(Q_m\)MCG = 24.4 mg g\(^{-1}\)).
mg·g⁻¹). Given the good agreement between model fit and experimentally tested equilibrium adsorption capacity in addition to the large correlation coefficients, it suggests that Mn²⁺ adsorption on the two adsorbents both followed Langmuir isotherms. The Langmuir constant \( k_l \) is a characteristic parameter related to the binding energy of solute and adsorbent. It reflects the spontaneity of the adsorption reaction. Namely, the greater the \( k_l \), the higher the spontaneous adsorption, and so the more stable the product and the better the adsorption capacity (Wang & Ariyanto 2007). In the experiment the \( k_l \) value is relatively low, which means the adsorption product of adsorbents and Mn²⁺ were not stable and easily to desorbed.

The favorability and feasibility of the adsorption process can be determined by the separation factor or equilibrium factor (RL) in the analysis of data by the Langmuir isotherm. The Langmuir constant \( k_l \) is a dimensionless separation factor. The value of RL indicates the shape of the isotherms to be either unfavorable (RL > 1), linear (RL = 1), favorable (0 < RL < 1) or irreversible (RL < 0). All the RL values calculated lie between 0 and 1 (RL-CG: 0.0187–0.0212; RL-MCG: 0.1167–0.1196) indicating that Mn²⁺ adsorption on the adsorbent samples is favorable.

### Adsorption kinetics

Adsorption kinetic models can be useful to determine the mechanism of adsorption and the efficiency of the adsorbents for the removal of pollutants. The pseudo-first and pseudo-second-order models have been widely applied to a number of metal/sorbent sorption systems. The linear form of the pseudo-first-order kinetic can be shown by Equation (6):

\[
\ln(Q_e - Q) = \ln Q_e - k_1 t
\]

where \( Q_e \) is the amount of solute adsorbed at equilibrium time (mg) and \( k_1 \) is the rate constant for pseudo-first-order (min⁻¹). \( Q_e \) and \( k_1 \) were determined from the slope and intercept of the linear plot of \( \ln (Q_e - Q) \) against \( t \), respectively.

The linear form of pseudo-second-order is described in the following Equation (7):

\[
\frac{t}{Q} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}
\]

where \( k_2 \) (g mg⁻¹ min⁻¹) is the pseudo-second-order rate constant. \( Q_e \) and \( k_2 \) can be determined from the intercept and slope of \( t/Q \) versus \( t \) in Equation (7), respectively.

The adsorption data versus adsorption time for Mn²⁺ adsorption are shown in Figure 12(a). It can be seen that the adsorption capacity of the adsorbent was increased over adsorption time. The adsorption of Mn²⁺ rapidly increased at the start-up period and gradually increased during the remaining adsorption time until equilibrium time. It may be due to the adsorption sites that are abundantly available at the beginning of the adsorption time, and adsorption gradually decreased with reduced adsorption sites. Compared to CG, it is seen that adsorptive capacity of MCG was significantly increased. This fact is related to the effect of activation by calcination and additive, which brings about the separation of the constituent layers of CG, so guaranteeing greater accessibility for the molecules of adsorbate (Cristóbal et al. 2009). The equilibrium time varied when adsorbent changes. The time to establish equilibrium for MCG was longer than for CG under the same condition. The equilibrium time for CG was reached in 30 min, whilst for MCG it was reached in 60 min. This is because calcination causes the transformation of kaolinite contained in CG into metakaolinite. The disorganized structure of metakaolinite hinders the interactions between the adsorbent material surface and the adsorbate molecules. All subsequent experiments were, therefore, conducted for a maximum period of 30 min for CG samples and 120 min for MCG samples. The results (Table 4 and Figure 12(b)) showed that the kinetic of adsorption

<table>
<thead>
<tr>
<th></th>
<th>( Q_e ) (exp) (mg·g⁻¹)</th>
<th>( Q_m ) (mg·g⁻¹)</th>
<th>( k_l ) (L·mg⁻¹)</th>
<th>( R^2 )</th>
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<td>MCG</td>
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<td>23.9</td>
<td>1.3</td>
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<td>0.1183</td>
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<td>3.2</td>
<td>2.1</td>
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### Table 3 | Langmuir and Freundlich isotherm parameters for Mn²⁺ adsorption

<table>
<thead>
<tr>
<th></th>
<th>( Q_m ) (mg·g⁻¹)</th>
<th>( k_l ) (L·mg⁻¹)</th>
<th>( R^2 )</th>
<th>RL</th>
<th>( n ) (g·L⁻¹)</th>
<th>( R^2 )</th>
</tr>
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<tbody>
<tr>
<td>MCG</td>
<td>0.401</td>
<td>4.01</td>
<td>0.0212</td>
<td>RL-MCG: 0.1167</td>
<td>0.401</td>
<td>2.4</td>
</tr>
<tr>
<td>CG</td>
<td>0.596</td>
<td>0.596</td>
<td>0.0192</td>
<td>RL-CG: 0.0187</td>
<td>0.596</td>
<td>1.7</td>
</tr>
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</table>
onto the two adsorbents adequately fitted the pseudo-second-order model, which usually describes not only the diffusion process but also the surface reaction process. This indicates that the limiting stage in the rate of adsorption is adsorption at the surface, which is dependent on availability of the adsorption sites, and points toward the chemical nature of the adsorbate-adsorbent interactions (De Sales et al. 2015). In other words, it has been suggested that the first process can be attributed to instantaneous occupation of most of the available surface sites on the MCG particles, and the negatively charged surface of the MCG would result in a very rapid rate of adsorption. The second process may be due to the gradual uptake of Mn\textsuperscript{2+} by the MCG particles by diffusion through pores (Qi et al. 2015).

Table 4 | Kinetic parameters for Mn\textsuperscript{2+} adsorption

<table>
<thead>
<tr>
<th>Pseudo-first-order</th>
<th>Pseudo-second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_m ) (mg g(^{-1}))</td>
<td>( k_1 ) (min(^{-1}))</td>
</tr>
<tr>
<td>CG 1.1</td>
<td>0.013</td>
</tr>
<tr>
<td>MCG 20.6</td>
<td>0.031</td>
</tr>
</tbody>
</table>

CONCLUSION

We developed a new calcination method to convert CG into a modified form called MCG. We found the MCG is a promising adsorbent to remove manganese ion (Mn\textsuperscript{2+}) residues from industrial wastewater. The concentration of Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}•10H\textsubscript{2}O, as the additive in the calcination process, was optimized along with the temperature of calcination. When Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}•10H\textsubscript{2}O (m/m) is 8% and the temperature is 500 °C, the MCG has the best adsorbent capacity for Mn\textsuperscript{2+}. During the calcination process, the decomposition of carbonate minerals leads to a porous structure of the surface of CG particle, and the addition of Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7}•10H\textsubscript{2}O improved the dehydration of CG particle to form a silicate network structure. Both effects increased the pore volume and specific surface area of MCG particle. Moreover, the transformation through a dehydration reaction of CG from kaolinite to metakaolinite also increased the adsorbent capacity of MCG. The maximal adsorptive capacity of Mn\textsuperscript{2+} on MCG was over seven times higher than that on CG. The adsorption behavior was found to follow the Langmuir isotherm model, and it is a favorable type. Furthermore, the pseudo-second-order kinetic analysis described the adsorption as a chemical interaction process. In view of the above, the low cost and high capability of
MCG makes it a potentially attractive adsorbent for eliminating Mn$^{2+}$ from aqueous solution.

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