Application of rice straw, corn cob, and lotus leaf as agricultural waste derived catalysts for low temperature SCR process: Optimization of preparation process, catalytic activity and characterization

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Abstract:

Carbon-based catalytic materials have received significant attention for low temperature flue gas denitrification (DeNO\textsubscript{x}) process, due to their physicochemical properties and ease of modification. To improve the DeNO\textsubscript{x} efficiency, preparation of biochar catalyst supports was conducted that included the acid treatment of the agricultural wastes rice straw, corn cobs and lotus leaves. Taguchi experimental design ($3^4$) was employed to screen suitable carbon materials and optimize the preparation parameters of the biochar. All of the acid-modified and unmodified samples were evaluated to determine their performance and they were characterized by using SEM, BET and FT-IR analysis. The experimental and characterization results showed that acid modification of the biochars improved their DeNO\textsubscript{x} performance, which may have been due to the changes in the physical and chemical properties of the carbon material following the acid treatment. The optimum combination in the acid modification procedure was found to be the use of lotus leaf carbon treated with an acid/mass ratio of 1.50 and a pyrolysis temperature of 800°C. The biochar prepared using these optimum preparation parameters were then employed as a carrier to support an active catalyst component (MnO\textsubscript{x}). The lotus leaf biochar supported 10 wt.% manganese catalyst prepared using ultrasonic impregnation method exhibited nearly 90% NO\textsubscript{x} conversion at 250 °C at a high space velocity of 45, 000 h\textsuperscript{-1}, and it exhibited strong resistance to H\textsubscript{2}O. Additional studies showed that higher redox capacity and suitable surface acidity were two of the deciding factors in the improved low temperature SCR performance of the 10%
Mn/LBC catalysts.

Keywords: Agricultural wastes; Acid modification; Low temperature flue gas denitrification; Carbon materials.

1. Introduction

Nitrogen oxides (NO$_x$) generated by fossil fuel combustion can produce a number of environmental problems, including urban haze, photo-chemical smog, acid rain, ozone depletion and greenhouse effects (Anenberg et al., 2012; Cheng et al., 2018; Huang et al., 2019; Mu et al., 2019). Fossil fuel combustion emissions of NO$_x$ from industrial and residential energy consumption over the last century have been the primary source of NO$_x$ in the atmosphere (Skalska et al., 2010). In addition, severe urban haze has recently become one of the most significant urban air quality issues, and NO$_x$ has been shown to be one of the most important precursors of this haze pollution (Anenberg et al., 2012). Consequently, removal of NO$_x$ from industrial flue gas has become an increasingly urgent task to improve urban ambient air quality (Skalska et al., 2010; Anenberg et al., 2012; Wang and Hao, 2012). Several techniques have been used for the elimination of NO$_x$ from flue gas including selective catalytic reduction (SCR), catalytic decomposition, liquid absorption and plasma catalysis. However, of these, SCR of NO$_x$ by NH$_3$ is one of the most effective flue gas cleaning technologies for stationary sources. The V$_2$O$_5$ – WO$_3$/TiO$_2$ commercial catalysts that form the basis of SCR technology have been widely studied and the SCR unit is always situated in front of the dust precipitation and desulphurization units in a treatment system (Bosch, 1988; Busea et al., 1998; Chen et al., 2018). The high operating temperature of
300–450°C and the toxicity of vanadium, limit its practical application as a commercial catalyst for industrial furnaces that emit low temperature flue gases (<250°C). This includes the coking industry, refuse incineration and coal-fired power plants (Li et al., 2011; Fu et al., 2014). Therefore, the necessity has developed to identify vanadium-free low temperature SCR catalysts that can be used to lower the \( \text{NO}_x \) emissions in these industries.

Carbon materials, including activated carbon, graphene, carbon nanotubes etc., have found wide application for use in low temperature SCR, because of their high specific surface areas and chemical stability (Marban et al., 2004; Lu et al., 2010; Zhu et al., 2011; Wang et al., 2012; Jiao et al., 2015; Yu et al., 2015). In particular, the manganese oxide catalysts have attracted great attention, because they contain various types of labile oxygen and oxidation states of Mn (Jiang et al., 2019b; Zhang et al., 2019; Tong et al., 2020; Wang et al., 2020). This improves the feasibility of the use of these catalysts to complete the catalytic cycle in low temperature \( \text{NH}_3 \)-SCR. Therefore, the combination of \( \text{MnO}_x \) and carbon materials could produce an ideal low temperature SCR catalyst. Moreover, many carbon-based low temperature SCR catalysts have been developed over the past 10 years that offer high low temperature SCR performance, but also have good anti-poisoning properties due to the hydrophobicity and special pore structure of carbon materials (Bai et al., 2010; Xiao et al., 2016; Yu et al., 2016; Dong et al., 2017). However, the high cost of these carbon materials continues to be the main impediment to their widespread use in \( \text{NO}_x \) removal processes (Zhu et al., 1999; Huang and Teng, 2003). Carbon materials can be
easily produced as pellets, which are cheaper to produce than honeycomb-shaped one.

Therefore, the challenge has been to find a cheaper carbon support for the SCR catalyst and then modify it to enhance its SCR catalytic performance. To date, its environmental benefits and abundance have convinced many researchers to devote their efforts to the production of activated carbon or other useful materials from various types of biomass (Jo et al., 2011), such as cotton stalks (Shen et al., 2015), peanut shell (Yang et al., 2018), rice straw (Cha et al., 2010), rice husk (Chen et al., 2019), etc. However, there have been few reported studies that have focused on the modification and optimization of the preparation of biochar from agricultural waste.

Using agricultural wastes for biomass energy recovery and air pollution control could also help to solve the problem of disposing of these agricultural wastes.

It has been found that a change in surface chemistry of modified carbonaceous materials affects their adsorption and catalytic properties (Boehm, 2002). Samojeden et al. (Samojeden et al., 2015) provided an overview of how to enhance DeNO_x performance of the carbon materials. A study reported by Zhou et al. also found that the HNO_3-modified AC could increase the abundance of various oxygen containing functional groups on the carbon surface, which was beneficial to the DeNO_x reaction (Zhou et al., 2007). Hence, it appears to be very important to modify the raw biochar materials to enhance their DeNO_x properties. However, the type of raw material and its nature also dictate the DeNO_x activity of resulting biochars (Cha et al., 2010; Ahmad et al., 2016). In addition, the nature and internal structure of the raw materials can affect the catalytic activity of the prepared biochar-based catalysts. Thus, a
comparative study of the preparation and modification of the various types of raw biomass charcoal is needed.

In this reported work, Taguchi experimental design ($3^4$) was employed to screen suitable carbon materials and optimize the preparation parameters of the biochar materials. In addition, the effect of acid modification on the low temperature flue gas DeNO$_x$ performance of these biochars was also studied. Moreover, the low temperature SCR performance of various raw biomass charcoals used in preparing MnO$_x$ supported catalysts was determined and the related structure-activity relationship between these materials was also investigated.

2. Experimental

2.1 Orthogonal design of catalysts

A Taguchi’s orthogonal array L9 was used for selection of the raw carbon materials and the methods for their modification. In this reported study, the carbon material type, pyrolysis temperature, acid type and dosage of acid were used as factors in orthogonal experiments. Each factor was set to three levels and an orthogonal table L9 ($3^4$) of was designed. Table 1 shows the various test factors and selected levels. Factor A was the carbon material type, which was either the rice straw, corn cob or lotus leaf. These starting materials were obtained from the experimental agricultural fields of Jiangxi Agricultural University. Factor B was the pyrolysis temperature for the preparation of the biochar, which was 600°C, 700°C and 800°C. Factor C was the type of acid used, which included nitric acid, phosphoric acid or
sulphuric acid. Factor D was mass ratio of acid to raw material, which was 0.75, 1.50 and 3.00. This experimental design reduced the number of runs needed to screen the candidate catalysts or catalyst supports from 27 runs to 9 runs.

2.2 Catalysts preparation

For comparison, three kinds of the biomass char were obtained from rice straw, corn cob and lotus leaf. All of the starting materials were dried for 12.0 h at 110°C and then pyrolyzed at a specified temperature for 2.0 h in a nitrogen atmosphere. The three carbon materials (rice straw, corn cob and lotus leaf) were then ground and sieved through 20-40 mesh screens, followed by washing with distilled water 5 times and drying at 110°C for 5.0 h. These three samples constituted the unmodified materials and were labeled CK. 1, CK. 2 and CK. 3. Proximate and ultimate analyses were also conducted using three kinds of agricultural waste (rice straw, corn cob and lotus leaf) as shown in Table 2.

In this experiment, Cat. 1 to Cat. 9 represent the acid modified samples. With the exception of the acid modification, all of the procedures used for the preparation of biochars were the same for the modified and unmodified material. The mass ratio of acid to biomass material for the modified samples was designated as $x$: 1 with $x = 3.00, 1.50, 0.75$. The acid modified samples were dispersed in a specific acid solution and stirred for 2.0 hours and completely impregnated the biochar with acid for 14.0 hours and then the material was filtered from solution. The filtered powders were dried at 105°C for 24.0 hours, and calcined in a tube resistance furnace at $y°C (y =$
600, 700, 800) for 2.0 h using a ramp rate of 5°C•min⁻¹ in N₂ atmosphere. After the activation, N₂ was continuously flowed through the furnace until the tube furnace tube reached room temperature to obtain the primary biochar product. Then, the samples were washed with deionized water until the wash water was neutral pH, and the washed samples were dried at 105°C. The final powders were used as the prepared biochar or biochar carriers in this study.

A series of z wt%/RBC, z wt%/CBC and z wt%/LBC catalysts (z = 0, 5, 10, 15) were prepared using the ultrasonic impregnation method. RBC, CBC and LBC represented rice straw biochar, corn cob biochar and lotus leaf biochar. A solution of manganese acetate was made with a constant Mn loading of z wt%. This solution was then added to a beaker containing an individual biochar. This mixture was sonicated for 0.5 h to affect complete dispersion of the biochar in the solution. After Mn impregnation, the samples were dried in air at 100°C for 12 h, and then calcined in a tubular furnace in N₂ at 400°C for 2 h. The specific preparation parameters of these catalysts are shown in Table 3.

2.3 NH₃-SCR activity measurement

The activity tests of the samples were performed in a fixed-bed quartz flow reactor at atmospheric pressure. A 40-60 mesh sample (1.6 mL) was placed in a fixed-bed quartz reactor (12 mm i.d. ×600 mm in length), and the reaction temperature was increased from 100°C to 300°C at a ramp rate of 5°C•min⁻¹. The feed gas composition was 0.06% NO, 0.06% NH₃, 2.5% O₂, 8.0 % H₂O (when used), balanced
with Ar. The total flow rate was 1200 mL•min\(^{-1}\), which corresponded to a space velocity (GHSV) of 45,000 h\(^{-1}\). The composition of the product gas was continually monitored using a Testo 350 NO-NO\(_2\)-NO\(_x\) flue gas analyzer (Testo Limited, Germany). The NO\(_x\) removal efficiency was calculated using the following equations:

\[
\text{NO}_x \text{ conversion}\% = 100 \times \left( \frac{C_{\text{NO}_x}^{\text{in}} - C_{\text{NO}_x}^{\text{out}}}{C_{\text{NO}_x}^{\text{in}}} \right)
\]  

(1)

where the subscripts "\text{C}^{\text{in}}" and "\text{C}^{\text{out}}" represent the inlet and outlet gas concentrations of NO\(_x\), respectively.

2.4 Characterization of catalysts

The morphology of the catalyst samples was studied using scanning electron microscopy (SEM) employing a HITACHI S-3400N instrument. The BET surface areas of the catalysts were measured using a Micromeritics ASAP 2020 analyzer (Micromeritics Instrument Corp., USA). The FT-IR spectra of the biochar samples were recorded using a Nicolet 6700 FTIR spectrometers and the FTIR spectra were obtained at a resolution of 4 cm\(^{-1}\).

3. Results and Discussion

3.1 SCR catalytic activity

The use of biochars derived from rice straw, corn cob and lotus leaf, which are normally disposed of as agricultural waste, was investigated as potential catalysts for low temperature selective catalytic reduction of NO\(_x\) by NH\(_3\). Three kinds of biochars were prepared using these three precursors employing a designed orthogonal
experiment (see Table 1). As seen in Fig. 1, the NO\textsubscript{x} conversions of the unmodified samples CK.1, CK. 2 and CK. 3 were all lower than 5% at a reaction temperature of 150°C, and the DeNO\textsubscript{x} activity of the unmodified samples (CK.1~CK.3) was also much lower than that of the modified samples (Cat. 1~Cat. 9). The NO\textsubscript{x} conversion rate of the acid modified carbon materials was significantly higher than that of the unmodified samples, indicating that the physicochemical properties of the carbon materials was altered by the acid modification process. This phenomenon was consistent with the research reported of Ren et al. (Ren et al., 2017) and Shen et al. (Shen et al., 2015). The NO\textsubscript{x} conversion of the acid modified rice straw biochar was lower than that of the other two kinds of acid modified biochar, which was less than 10%. However, the NO\textsubscript{x} conversion by the acid modified lotus leaf biochar was more than 17% greater, and overall level of the DeNO\textsubscript{x} rates of these biochars was relatively high. The optimum result of 21.0% conversion by the lotus leaf biochar was obtained using Cat. 7, which was processed using sulphuric acid. However, of the 12 sets data shown in Fig. 1, Cat. 6 (corn cob), which was prepared at 800°C using nitric acid, exhibited the best DeNO\textsubscript{x} result. These data together with the variable analysis of the orthogonal experiments can provide the optimum preparation parameters of the biochar material for flue gas DeNO\textsubscript{x} at low temperature. A detailed analysis of this process is included in Section 3.2.

### 3.2 Variance analysis of the orthogonal experiments

Based on the of the activity evaluation, an orthogonal test method was used to
determine the effect of carbon material type, pyrolysis temperature, acid type and weight ratio (acid/raw material) on the DeNO$_x$ rate of prepared biochar materials. Each of the samples was tested at three levels and orthogonal experiments L9 (3$^4$) were used to screen the optimum preparation parameters for producing the biochar. The orthogonal experimental results are shown in Table 4. As can be seen from these data, the DeNO$_x$ rates of the corn cob biochar and lotus leaf biochar were higher than the results obtained using the rice straw biochar. The maximum DeNO$_x$ rate for rice straw biochar was 8.81%, the minimum DeNO$_x$ rates of the corn cob bio-char and the lotus leaf biochar were 15.06% and 17.79% respectively. The DeNO$_x$ rate of all the rice straw bio-char samples was very low, which may have been related to the large amount of inert Si in these samples. The highest DeNO$_x$ rates for the three carbon materials (rice straw, corn cob and lotus leaf) were 8.81%, 22.12% and 21.15%, respectively. This indicated that lotus leaf bio-char or related derived catalysts exhibited good potential for application in a low temperature flue gas DeNO$_x$ process.

The range analysis results for the DeNO$_x$ rate are listed in Table 5. The value of the range of Factor A (carbon material type) was 36.22, which was the maximum of the four factors. The second highest was Factor C (acid type) with a value of 10.42. The third was Factor D (dosage) had a value of 9.62. Therefore, the order of the influencing factors on the DeNO$_x$ rate in sequence was A>C>D>B. For Factor A, A3 with a value of 56.73 was optimum, C1 was best a value of 48.72, D2 was best with a value of 48.72 and B3 was best with a value 46.16 was optimum for DeNO$_x$ rate, respectively (see Fig. 2). The variance analysis results are provided in Table 6. The F
values for Factor A, Factor B, Factor C and Factor D were 23.77, 1.00, 1.65 and 1.47, respectively. When the Significance $\alpha = 0.05$, $F_{\alpha > F_{0.05}} (2, 2) = 19$. Therefore, Factor A was the most significant in the DeNO$_x$ rate and the impact of Factor B, C and D on the DeNO$_x$ rate of the biochar material was very limited. The variance analysis results were in agreement with the results of the range analysis. For acid modification, the optimum combination for the DeNO$_x$ experimental was A3C1D2B3, in other words, lotus leaf carbon material, nitric acid, an acid/mass ratio of 1.50 and a pyrolysis temperature of 800°C.

3.3 Characterization of the biochar

3.3.1 SEM analysis

Fig. 3 shows the SEM micrographs of rice straw samples with and without acid modification. The effect of acid modification on the surface morphology of the straw biochar was quite obvious. The CK. 1 sample (Fig. 3a&b) was also prepared by pyrolysis at 700°C under N$_2$ atmosphere conditions with no acid modification. As can be seen in this micrograph, impurities and fragments are present on the non-acid modified rice straw biochar materials, which appeared bar-like or wire-like shapes. This phenomenon was also reported by Peng et al. (Peng et al., 2011). Following acid modification, the surface morphology of the acid modified rice straw biochar (Cat. 1; Fig. 3c&d) was more regular than the non-acid modified sample. In addition, the SEM images revealed that the biochar consisted of irregular spherical bulges with a porous structure, which provided effective catalyst adsorption sites. Considering that its
DeNO\textsubscript{x} performance was improved after acid modification, it was concluded that the small spherical bulges on the biochar surface may have been the reason for the improvement in the catalytic activity of the material.

Fig. 4 shows the SEM micrographs of the corn cob samples before and after acid modification. The CK. 2 biochar sample (Fig. 4a & b) was prepared by pyrolysis at 700°C under N\textsubscript{2} atmosphere conditions. The surface of this sample appears to have very few channels with significant amounts of debris on the surface. Fig. 4c & d are SEM micrographs of the corn cob biochar material, which appears to show an ordered honey-comb structure of macropores measuring 5-15 \( \mu \)m in diameter, separated by relatively thick (2-4 \( \mu \)m) pore walls. However, the morphology of the CK. 2 biochar sample (Fig. 4a & b) is very different. After acid modification, regular and orderly channels can be clearly seen on the SEM images of the Cat. 6 sample (Fig. 4c & d). It can be inferred from this result that the higher pyrolysis temperature and acid treatment were beneficial to the formation of biochar pore channels in the corn cob.

Fig. 5 shows the SEM micrographs of lotus leaf biochar samples before and after acid modification. As can be seen from these images (Fig. 5a & b), the CK. 3 sample surface appears to be a porous, folded structure with attached carbon material debris. After acid modification, it appeared that the surface of the Cat. 7 sample (Fig. 5c & d) had changed exhibiting more cavities with less debris on the acid modified lotus leaf biochar. In addition, the acid modified Cat. 7 had more folds and layers than the unmodified sample. Huang et al. also prepared a lotus-leaf-based carbon without acid modification that produced a carbonaceous product without channels and cavities
(Huang et al., 2018). It may be that the oxidation reactions induced by the acid produced a porous structure and removed the debris and impurities from the lotus-leaf biochar. Considering that the DeNO$_x$ performance of the lotus leaf biochar improved after acid modification, it is apparent that less debris and abundant channels and cavities on the surface of biochar may be the reason for the improved catalytic performance of the product.

3.3.2 BET analysis

The specific surface area, pore volume, and pore size distribution of the biochar materials are listed in Table 7. For the three unmodified biochar material, their specific surface area and pore volume were less than 22.00 m$^2$•g$^{-1}$ and 0.06 cm$^3$•g$^{-1}$ respectively, which was less than the values for the acid modified carbon materials with acid modification. These results suggested that the relatively low specific surface area and pore volume of the unmodified materials was connected their low DeNO$_x$ rate. However, average pore size of the unmodified carbon materials was relatively large and the overall level of the average pore size of these modified carbon materials was much smaller than the pore sizes of the unmodified carbons. This suggested that the acid oxidation acid of the biochar produced smaller pores in the modified carbon.

In contrast to raw carbon materials, after acid modification, the specific surface area and pore volume of the acid modified carbon materials were both higher than 110.00 m$^2$•g$^{-1}$ and 0.09 cm$^3$•g$^{-1}$ respectively. The highest and lowest the specific surface area was found in the Cat. 5 sample (409.67 m$^2$•g$^{-1}$) and Cat. 6 sample (115.24 m$^2$•g$^{-1}$), which were derived from corn cob. These results suggested that the
physical indices of the corn biochar were greatly affected by the conditions of the acid modification (i.e., acid type, dosage of acid, etc.). In the case of the samples with a good DeNO\textsubscript{x} rate (Cat.6: 22.12% and Cat.7: 21.15%), the specific surface area (Cat.6: 115.24 m\textsuperscript{2}•g\textsuperscript{-1} and Cat.7: 211.88 m\textsuperscript{2}•g\textsuperscript{-1}) and pore volume (Cat.6: 0.110 cm\textsuperscript{3}•g\textsuperscript{-1} and Cat.7: 0.157 cm\textsuperscript{3}•g\textsuperscript{-1}) of these two samples was not the highest. However, the average pore size of these two samples was relatively high. This suggested that the DeNO\textsubscript{x} performance of carbon materials was also related to other factors including surface chemical functionality. Other researchers have also reported that the DeNO\textsubscript{x} rate of carbon materials is dependent on surface chemistry (Ren et al., 2017; Yu et al., 2017a).

To sum up, the acid modification process changed the physical properties of the carbon materials, and these changes appeared to improve the SCR performance of the resulting carbon material products.

### 3.3.3 FT-IR analysis

To better understand the effect of acid modification on the surface chemical functional groups of the carbon materials, the experimental carbons were subjected to FTIR analysis. The FT-IR results for the experimental carbon materials with and without acid modification are shown in Figs. 6, 7 & 8. Based on previous studies (Gao and Moffat, 1995; Dandekar et al., 1998; Guo et al., 2015; Yu et al., 2015; Ren et al., 2017), the FT-IR bands at 3500–3200 cm\textsuperscript{-1} were due to OH stretching vibrations; the FT-IR bands at 1585 cm\textsuperscript{-1} was attributed to the C=C stretching vibration in aromatic compounds; the FT-IR bands at about 1093 cm\textsuperscript{-1}, 797 cm\textsuperscript{-1} and 460 cm\textsuperscript{-1} appeared to be due to Si-O-Si stretching vibration and the FT-IR bands at 973 cm\textsuperscript{-1} were attributed
to P-OH species.

The FTIR spectra of selected rice straw biochar samples prepared by different modification parameters are shown given in Fig. 6. As can be seen in Fig. 6, the peak at 1585 cm\(^{-1}\) is corresponds to the C=C stretching vibration in aromatic compounds. This suggests that the aromatic compounds in the rice straw did not completely decompose at this relatively low pyrolysis temperature. Consequently, trace amounts of aromatic compounds remained in the Cat.1 sample, which produced an absorbance peak at around 1600 cm\(^{-1}\). Three additional peaks at about 1093 cm\(^{-1}\), 797 cm\(^{-1}\) and 460 cm\(^{-1}\) appeared to be due to Si-O-Si stretching vibration. The presence of Si in the rice straw biochar is understandable, because Si promotes the growth of rice. The CK.1 sample was not acid modified, and the absorbance bands at 1093 cm\(^{-1}\) and 797 cm\(^{-1}\) were not present in the FTIR spectra of the CK.1 sample. Therefore, it was concluded that some Si could be retained in the biochar after acid modification.

The FTIR spectra of select corn cob biochar samples prepared by different modification parameters are shown in Fig. 7. As can be seen in Fig. 7, broad absorbance bands appeared at about 3400–3500 cm\(^{-1}\), which were assigned to the O-H stretching vibration of the hydroxyl functional groups. The absorbance band that appeared at 973 cm\(^{-1}\) in spectrum of the Cat. 4 sample may have been due to the stretching vibration of P-OH species. The band at around 450–460 cm\(^{-1}\) could be attributed to the Si-O-Si stretching vibration. After acid modification, it was concluded infer that some Si-O-Si species was retained in the material after acid modification.
The FTIR spectra of selected lotus leaf biochar samples prepared by different modification parameters are shown in Fig. 8. As can be seen in Fig. 8, the broad band at about 3400–3500 cm\(^{-1}\) in all the spectra was due to the O-H stretching vibration of the hydroxyl functional groups. The peaks at 1585 cm\(^{-1}\) and 1430 cm\(^{-1}\) correspond to the C=C stretching vibration in aromatic compounds and COH in-plane bending modes respectively. Compared to samples CK. 3 and Cat. 7, it was found that after acid modification the –COOH related functional groups were present, and the C=C functional groups disappeared. In addition, the intensity of the absorbance of the –COOH related functional groups for Cat. 7 sample was higher than CK.3. Considering that the NO\(_x\) removal rate of Cat.7 was much higher than the CK.3, it was concluded that the appearance of -COOH groups after acid modification may be a reason for the increase of NO\(_x\) removal rate of Cat. 7.

Fig.1 shows the high NO\(_x\) removal rate of Cat.7, which may be related to the fact that this catalyst had two surface functional groups (-COOH and -OH). Also, the carboxyl, anhydride and phenol groups have also been shown to be responsible for promoting NH\(_3\) adsorption during the DeNO\(_x\) process (Zhou et al., 2007; Guo et al., 2015). To summarize, after acid modification, there was an increase in variety and quantity of surface acidic functional groups on the biochar, which improved the adsorption of NH\(_3\). The DeNO\(_x\) performance of acid-modified biochar was significantly improved, which may be due to the change of physical and chemical properties of the carbon material after acid modification.
3.4 Low temperature SCR performance of the supported biochar catalysts

Orthogonal experimental results suggested that the optimum preparation conditions for the biochar materials were biochar carbon material, nitric acid, an acid/mass ratio of 1.50 and a pyrolysis temperature of 800°C. It has been well documented over the past several years that MnOₓ based catalysts provide high low temperature SCR performance compared with other metal oxides (Liu et al., 2016; Lee et al., 2017; Liu et al., 2017). In this reported work, the optimum carbon biochar material was used as a carrier to support the active catalyst component (MnOₓ). The low temperature DeNOₓ performance of the LBC based catalysts with different Mn loading (theoretical load: 0~15%) is shown in Fig. 9 as a function of temperature. The 10% Mn/LBC catalysts exhibited the best low temperature SCR performance in comparison to the other sample catalysts. The highest the NOₓ conversion values of the 10% Mn/LBC catalysts was achieved when the reaction temperature was 250°C. This performance is slightly better than results reported in the literature (Cha et al., 2010; Shen et al., 2015). Below 250°C, the activity of the catalyst increased monotonously with the reaction temperature, and when the reaction temperature was higher than 250°C, the SCR activity of the 10%Mn/LBC catalysts began to decrease. A similar phenomenon has also been observed in the studies of Wang et al. (Wang et al., 2012) and Su et al. (Su et al., 2013). This is because the oxidation of NH₃ readily occurs on the surface of the catalyst at relatively high temperatures. However, the highest NOₓ conversion values of 5% for the Mn/LBC and 15% for the Mn/LBC catalysts were both lower than 70%, which may have been related to chemical state of
Mn and surface acidity of the catalysts.

Ren et al. (Yang et al., 2018) used peanut shell bio-char as a support for manganese oxide to form an SCR catalyst and evaluated its activity. Their results showed that the NO\textsubscript{x} conversion rate of this catalyst was about 80% at 250 °C. A Mn loading of 10 wt.% on the biochars reported in this current study was found to be mainly responsible for the observed DeNO\textsubscript{x} rate, which was better than that detailed in previously reported work (Singh et al., 2013; Yang et al., 2018).

Finally, the SCR activities as a function of temperature of the 10% Mn/RBC, 10% Mn/CBC and 10% Mn/LBC catalysts were obtained, as shown in Fig. 10. The best low temperature SCR performance of these three samples was also found in the 10% Mn/LBC catalysts. The low temperature SCR performance of the other two catalysts was relatively low, which was less than 75% NO\textsubscript{x} conversion.

3.5 Characterization of catalysts

3.5.1 SEM analysis

Surface morphologies of lotus leaf biochar and 10% Mn/LBC catalyst are shown in Fig. 11 (a & b) and the EDX results for the 10% Mn/LBC catalyst are also presented in Fig. 11 (c & d). As shown by these results, the surface of the lotus leaf biochar prepared by acid modification was relatively clean and the structure was quite porous which favored gas adsorption and reaction. When compared to the material shown in Fig. 11 (a & b), it can be seen that when the modified lotus leaf biochar was loaded with MnO\textsubscript{x} its surface roughened, possibly as a result of the dispersion of the active component and the subsequent calcination process. Moreover, many fragments
or granular materials appear on the surface of the lotus leaf biochar after loaded with active MnOx. This phenomenon could be attributed to the active component (MnOx) supported on the surface of biochar as confirmed by the EDX results (Fig. 11 c & d). Also, as illustrated in Fig. 11 (c & d), the mass fraction of manganese in selected areas was about 21.8%, which suggests that dispersion process was efficient and manganese oxide dispersed on the surface of biochar carrier.

3.5.2 H2-TPR analysis

H2-TPR tests were conducted on the 10% Mn/RBC, 10% Mn/CBC and 10% Mn/LBC catalysts to determine the reducibility of metal species in the catalyst and the results are shown in Fig. 12. As shown in this figure, the Mn/biochar catalysts exhibited two redox peaks at 360~380°C and 540~560°C, which correspond to the reduction of MnO2 or Mn2O3 to Mn3O4, and Mn3O4 to MnO, respectively (Su et al., 2013). A very weak shoulder peak at about 230~230°C was also found and was attributed to the reduction of the easily reducible surface oxygen species (Yu et al., 2017b). Often, the redox ability of a catalyst is closely associated with its low temperature SCR activity, and the stronger the redox capability, the higher the SCR activity (Zuo et al., 2014; Liu et al., 2019; Wang et al., 2020). Comparing the peak positions of these biochar catalysts (Fig. 12), the temperature (336°C) that corresponds to the center of reduction peak of the 10% Mn/LBC catalyst was lower than that of the other catalysts which was an indication of the good low-temperature SCR activity of the 10% Mn/LBC catalyst. Also, the center of reduction peak of the 10% Mn/LBC catalyst was much lower than that of the other bio-char catalysts as reported by Wu et al. (Wu et al., 2012). Moreover, the temperature that corresponded
to the reduction peak center for these catalysts (10% Mn/LBC < 10% Mn/CBC <10% Mn/RBC) could be correlated to the low temperature SCR activity of these catalysts (10% Mn/LBC > 10% Mn/CBC >10% Mn/RBC).

3.5.3 NH₃-TPD analysis

The capacity of a catalyst to adsorb NH₃ or activate NH₃ is an important mechanism in the low temperature DeNOₓ process (Bosch, 1988; Busca et al., 1998; Chen et al., 2018), and is thought to be governed by respective presence of Lewis and Brönsted acid sites. Fig. 13 shows the NH₃-TPD results of the three types of biochar supported 10% Mn catalysts where it can be seen that the biochar based catalysts appeared to exhibit similar NH₃ desorption curves. The amount of NH₃ adsorbed by the catalysts was in the order of: 10% Mn/CBC > 10% Mn/LBC > 10% Mn/RBC. It was noted that there was a shift in the peak positions of the various catalysts, from which it was concluded that the acid strength of the 10% Mn/CBC catalysts decreased slightly. However, the amount of acid sites of the 10% Mn/CBC catalysts was the highest, while the amount of acid sites of the 10% Mn/RBC catalysts was the lowest, which was obtained by calculating the area under the desorption peaks. Also, the amount of acid sites of 10% Mn/LBC was between that of 10% Mn/CBC and 10% Mn/RBC. Considering the SCR activities of these catalysts, it was suggested that that a suitable surface acidity of the catalysts was one of important reasons for the good SCR performance of supported Mn-based catalysts at low temperature. Comprehensive analysis of the surface acidity and redox performance of the biochar based catalysts, it shows that the redox performance of each catalyst is relatively different and the catalyst with stronger redox performance has better SCR
performance at low temperature. This is consistent with the conclusion that redox capacity of the catalyst is the key to ensure the low temperature activity of the catalyst, which is has been reported in many literatures (Li et al., 2011; Jiang et al., 2019a; Jiang et al., 2019b; Wang et al., 2019).

3.6 H₂O resistance test

Recently, low temperature NH₃-SCR catalysts, such as Mn based catalysts, have attracted the attention of an increasing number of researchers, because they are suitable for a tailend position that can protect catalysts from high concentration of dust (Tong et al., 2020). However, water tolerance of the catalyst is a newly identified problem, which can be ignored at high temperature (Jiang et al., 2018; Han et al., 2019; Wang et al., 2019; Zhang et al., 2019). Therefore, water tolerance tests were performed on the 10% Mn/RBC, 10% Mn/CBC and 10% Mn/LBC catalysts and the results as a function of time are shown in Fig. 14. As shown in this figure, the NOₓ conversion of the 10% Mn/LBC catalysts attained a stable level of about 79.0% and proceeded for more than 120 min. However, The NOₓ conversion of the other two catalysts decreased with the amount of H₂O (8 vol%) in the inlet gas, where the SCR activity of the 10% Mn/RBC, 10% Mn/CBC decreased from 45% to 33% and from 68% to 53% respectively. However, the DeNOₓ rates quickly recovered after the H₂O was removed from the inlet gas. This shows the recoverable activity of the catalysts in the low temperature SCR system. Consequently, it can be concluded from these results that the inhibition effect of H₂O was attributed to the competitive adsorption of H₂O.
and NH₃ onto the catalyst surface. The possible reasons for this phenomenon were: (1) the active MnOₓ in the 10% Mn/LBC catalysts was high dispersed, which allowed for more active sites in NH₃-SCR reaction; and (2) carbon material itself possessed significant hydrophobicity. To summarize, the 10% Mn/LBC catalysts offered better resistance to H₂O than the catalysts.

4. Conclusions

In this reported work, the main conclusions were as follows:

(1) The optimum preparation conditions for biochar were successfully determined using an orthogonal experiment L9 (3⁴). After acid modification, the changes of surface physics and chemical characteristics of the biochar material appeared to improve the DeNOₓ rates of the material. The optimum carbon material was found to be lotus leaf that was treated with nitric acid (acid/mass ratio of 1.50) and pyrolyzed at a temperature of 800°C. The DeNOₓ rate of the lotus leaf biochar prepared using the optimum preparation parameters was as high as 22.5%. A select specific surface area and larger pore size played important roles in the DeNOₓ process, but the other factors also impacted the low temperature SCR performance of the material. The significance order of the three factors was: A3 (carbon materials type, lotus leaf) > C3 (acid type, nitric acid) > D2 (acid/mass ratio, 1.50) > B3 (pyrolysis temperature, 800°C). Overall, acid modification played an important role in improving SCR activity of biochar materials.

(2) Using agricultural wastes to prepare biochars, and this optimized carbon material was used as the carrier for an active component (MnOₓ). The 10% Mn/LBC
catalysts were prepared by the ultrasonic impregnation method. The 10\% Mn/LBC catalyst exhibited nearly 90\% NO\_x conversion at 250 °C at a high space velocity of 45,000 h\(^{-1}\), but also provided strong H\(_2\)O resistance at a reaction temperature of 250°C.

**Acknowledgement**

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**References**


Figure Captions

Fig. 1. NO$_x$ removal rate of these biochars before and after acid modification; Reaction conditions: 0.06% NO, 0.06% NH$_3$, 2.5% O$_2$, Ar balance, 150°C

Fig. 2. Effect of each design parameter on the DeNO$_x$ rate; “CC” refers to corn cob, the “LL” refers to lotus-leaf, “RS” refers to rice straw, “NA” refers to nitric acid, “PA” refers to phosphoric acid and “SA” refers to sulphuric acid

Fig. 3. SEM images of selected rice straw biochar; CK1:a & b, Cat. 1:c & d

Fig. 4. SEM images of selected corn cob biochar; CK 2:a & b, Cat. 6:c & d

Fig. 5. SEM images of selected lotus leaf biochar; CK 3:a & b, Cat. 7:c & d

Fig. 6. FT-IR spectra of the selected rice straw biochar samples

Fig. 7. FT-IR spectra of the selected corn cob biochar samples

Fig. 8. FT-IR spectra of the selected lotus leaf biochar samples

Fig. 9. Low temperature SCR performance for Mn/LBC with different Mn loading

Fig. 10. Low temperature SCR performance for three kinds of biochar supported MnO$_x$

Fig. 11. SEM results of the lotus leaf bio-char (a) and 10% Mn/LBC catalyst (b, c & d)

Fig. 12. H$_2$-TPR results for three kinds of biochar supported 10%Mn catalysts

Fig. 13. NH$_3$-TPD results for three kinds of biochar supported 10%Mn catalysts

Fig. 14. Effect of H$_2$O on SCR activity of catalysts: reaction conditions: 0.06% NO, 0.06% NH$_3$, 2.5% O$_2$, 8% H$_2$O, 250°C, Ar balance.
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Table 1. Orthogonal experimental design of acid modification experiments

Table 2. Proximate analysis and ultimate analysis of raw material

Table 3. The specific preparation parameters of these catalysts

Table 4. Orthogonal results of acid modification

Table 5. Range analysis results of DeNO_x rate

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Table 7. BET data for the biochar material

Table 1. Orthogonal experimental design of acid modification experiments

<table>
<thead>
<tr>
<th>Factors</th>
<th>A (Carbon material type)</th>
<th>B (Pyrolysis temperature/°C)</th>
<th>C (Acid type)</th>
<th>D (Dosage of acid/mass ratio)</th>
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<tr>
<td>Level</td>
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<td></td>
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<td>Nitric acid</td>
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<td>Nitric acid</td>
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<td>Cat. 3</td>
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### Table 2. Proximate analysis and ultimate analysis of raw material

<table>
<thead>
<tr>
<th>Sample</th>
<th>Proximate analysis (wt%)</th>
<th>Ultimate analysis (wt%)</th>
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<td>Rice straw</td>
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<td>Corn cob</td>
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<td>Lotus leaf</td>
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### Table 3. The specific preparation parameters of these catalysts

<table>
<thead>
<tr>
<th>Factors</th>
<th>A (Carbon material type)</th>
<th>B (Pyrolysis temperature/°C)</th>
<th>C (Acid type)</th>
<th>D (Dosage of acid/mass ratio)</th>
<th>Theoretical loading of active components</th>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>Corn cob</td>
<td>700</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CK. 3</td>
<td>Lotus leaf</td>
<td>700</td>
<td>-</td>
<td>-</td>
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<td>Optimized Catalysts</td>
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<td>OP.2(Pure CBC)</td>
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<td>10% Mn</td>
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<td>OP.3(Pure LBC)</td>
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<td>Nitric acid</td>
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<td>10%Mn/RBC</td>
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<td>10% Mn</td>
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<td>10%Mn/CBC</td>
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<td>Nitric acid</td>
<td>1.50</td>
<td>10% Mn</td>
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<td>10%Mn/LBC</td>
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<td>Nitric acid</td>
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<td>10% Mn</td>
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<tr>
<td>5%Mn/LBC</td>
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<td>5% Mn</td>
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### Table 4. Orthogonal results of acid modification

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<th>Experiment no.</th>
<th>A (Carbon material type)</th>
<th>B (Pyrolysis temperature/°C)</th>
<th>C (Acid type)</th>
<th>D (Dosage of acid/mass ratio)</th>
<th>DeNO\textsubscript{X} rate (%)</th>
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<td>Cat. 1</td>
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### Table 5. Range analysis results of DeNO\textsubscript{x} rate

<table>
<thead>
<tr>
<th>Index</th>
<th>A (Carbon material type)</th>
<th>B (Pyrolysis temperature/°C)</th>
<th>C (Acid type)</th>
<th>D (Dosage of acid/mass ratio)</th>
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<tr>
<td>K1</td>
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<td>K2</td>
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<td>38.30</td>
<td>48.72</td>
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<td>K3</td>
<td>56.73</td>
<td>46.16</td>
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<td>39.10</td>
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<tr>
<td>Range</td>
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<td>7.54</td>
<td>10.42</td>
<td>9.62</td>
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Range size: A>C>D>B

Optimal scheme: A3C1D2B3

### Table 6. Variance analysis results of DeNO\textsubscript{x} rate

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<tr>
<th>Variance source</th>
<th>Deviance quadratic sum</th>
<th>Degree of freedom</th>
<th>Mean square</th>
<th>F value</th>
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<tr>
<td>A</td>
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<td>130.91</td>
<td>23.77</td>
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<tr>
<td>B</td>
<td>11.01</td>
<td>2</td>
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<td>1.00</td>
</tr>
<tr>
<td>C</td>
<td>18.21</td>
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<td>D</td>
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<td>Total</td>
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### Table 7. BET data for the biochar material

<table>
<thead>
<tr>
<th>Sample</th>
<th>(S_{\text{BET}}) (m(^2)•g(^{-1}))</th>
<th>(V_{\text{total}}) (cm(^3)•g(^{-1}))</th>
<th>Average pore size (Å)</th>
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<tbody>
<tr>
<td>Cat. 1</td>
<td>218.370</td>
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<td>Cat. 2</td>
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<td>Cat. 3</td>
<td>321.310</td>
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<td>Cat. 4</td>
<td>312.700</td>
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<td>Cat. 5</td>
<td>409.670</td>
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