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1 **On preparation of biochar via pyrolysis at laboratory and pilot-**
2 **scales for removing antibiotics and immobilizing heavy metals in**
3 **livestock feces**

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Abstract

Purpose Pyrolysis is the most effective way to completely remove antibiotics and immobilize heavy metals from livestock feces. However, the effect of pyrolysis temperature on antibiotics removal at laboratory and pilot-scales is still unclear.

Materials and methods The pyrolysis technique was used to convert pig manure (PM) and chicken manure (CM) into biochar at different temperatures from 300 to 700 °C in the laboratory-scale test. The performances of antibiotics removal and heavy metals immobilization in livestock feces were studied. Therefore, the optimal temperature of 600 °C was selected for pilot-scale verification.

Results and discussion The results showed the removal of antibiotics of Tylosin (TYL), Tetracycline (TC), Chlortetracycline (CTC), Doxycycline (DOXY), Sulfamethazine (SMZ), Sulfadiazine (SDZ) and Sulfamethoxazole (SMX) was satisfactory, with all of the seven typical antibiotics totally removed at 600 °C. The heavy metals of zinc (Zn), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), cadmium (Cd) and arsenic (As) in the manures were well immobilized as well, while higher temperatures (above 600 °C) favored their immobilization. The results in heavy metals immobilization and antibiotics removal of pilot-scale test were similar to that of the laboratory test.

Conclusions Laboratory and pilot-scale studies showed that the current study provides a safe method and technology for treating and recycling livestock feces into biochar via pyrolysis process.

Keywords Livestock feces; Pyrolysis; Biochar; Antibiotics removal; Heavy metals immobilization; Pilot-scale.

1. Introduction

With the development of economy and increase in living standard, more and more livestock products are consumed, which leads to the results of large amounts of livestock feces. It was reported that about 250 million tons of livestock feces were produced annually in China (Yang et al. 2017). These manures will cause serious environmental problems if without proper treatments. For example, the manure contains high content of nitrogen and phosphorus, which can pollute the air and underground water if discharged directly. In the past, the manure was directly used as organic fertilizer to enhance the growth of crops (Feng et al. 2018). However, the new environmental issues concerned on manures occurred during applying and treating livestock feces. With the huge demand of livestock products, many additives with excess trace elements (especially Cu and Zn) and antibiotics were added in feeds to avoid diseases and enhance growth (Qiao et al. 2012; Wang et al. 2013). Most of the heavy metals and antibiotics added in feeds cannot be totally absorbed by livestock and then excreted via manures (Zeng et al. 2018; Zhou et al. 2019), which increased obviously the potential environment risks. Both the heavy metals and antibiotics pose a threat to environment and human health seriously.

Currently, valuable products generation and energy recovery from livestock feces with simultaneous safe treatment attract much attention and interests. In terms of different livestock feces treatment approaches, pyrolysis presents obvious advantages and has been well used for the dispose of sewage sludge and other kinds of solid wastes with additional targets of biochar generation, nutrient recycling and heavy metals immobilization (Yargicoglu et al. 2015; Troy et al. 2013; Wang et al. 2016). The obtained biochar that has many special characteristics can also be further utilized. For example, it was used to remove pollutants in water and soil as effective sorbent,

improve fertility and grain yield as soil amendment and enhance sewage sludge dewaterability as skeleton structure. (Ehsan et al. 2014; Tan et al. 2017; Li et al. 2018b).(Khorram et al. 2016; Zhang et al. 2016). (Xie et al. 2019). Some other researches were conducted to investigate the effect of pyrolysis on heavy metals immobilization during manures treatment. Lin et al. (2017) studied the impact of various pyrolysis temperatures on the speciation, leachability and bio-accessibility of Cu and Zn in animal manure-derived biochar. Zeng et al. (2018) reported the performance of different heavy metals during swine and goat manures pyrolysis, and found that the heavy metals were well immobilized after pyrolysis and higher temperature favored better performance. Other researchers found that the biochar could immobilize and adsorb the heavy metals in soil (Uchimiya and Bannon 2013; Ehsan et al. 2014), supplying useful approach for biochar application. In terms of another tough problem of antibiotics in livestock feces, the composting treatment can effectively reduce the antibiotics and part of antibiotics resistance genes. While, it is difficult to remove the antibiotics thoroughly, because some kinds of antibiotics cannot be degraded completely during compost due to their steady molecular structure (Pruden et al. 2013). Another question is if composting and fermentation eliminate some antibiotic and resistance genes, and then must resulting another stronger microbes and resistance genes (Zhou et al. 2019a). How can these new stronger microbes and resistance genes be eliminated to ensure human safety? Our previous study proved that converting pig manure into biochar could successfully decline the antibiotic resistance genes (Zhou et al. 2019b), which indicated that the antibiotics could be completely decomposed under rigorous pyrolysis conditions, and further obviously reduced the environmental pollution caused by antibiotics.

However, there were little researches on the effect of pyrolysis temperature on

the removal of antibiotics in livestock feces pyrolysis. In addition, although heavy metals immobilization during pyrolysis process was studied by some researchers, there was little information on pilot-scale verification under optimized pyrolysis condition to supply operational information for the industrialization. Therefore, the following contents were deeply studied in this work: (1) Effect of pyrolysis temperature on the removal of antibiotics in PM and CM. (2) Immobilization performance of heavy metals in the biochar samples obtained from PM and CM. (3) Pilot-scale verification under optimal pyrolysis condition. In general, this work gives comprehensive investigation in simultaneous antibiotic removal and heavy metals immobilization during PM and CM pyrolysis from laboratory-scale research to pilot-scale verification.

2. Materials and Methods

2.1. Materials and biochar characterization

The used PM and CM were obtained from a livestock and poultry farm in Xiamen and Zhangzhou, respectively, Fujian province, China. The PM and CM were smashed to 100 mesh (0.15mm) after freeze dried at -55 °C for 24 h to remove moisture, then stored at a dryer for further analysis and tests.

The ultimate analysis of the PM, CM and their biochar samples were measured using an elemental analyzer (VARIO MAX, Germany), and the proximate analysis was tested according to the Chinese standard methods (GB/T 28731-2012). A pH meter (Denver, UB-7, USA) was operated to get the pH of raw and biochar samples. The textural parameters of the raw and biochar samples were measured via BET-N₂ (ASAP-2020, USA), and the FT-IR spectrometry (iS10, Thermo, USA) was applied to analyze the surface functional groups of the raw and biochar samples. The thermal properties of different antibiotics were measured in a thermogravimetric analyzer (TG

209 F3, Netzsch, Germany), and the detail supplemental information of the seven different antibiotics was listed in Table S1. All the heavy metals contents were tested by the inductively coupled plasma mass spectrometry (ICP-MS Agilent 7500cx, USA). The concentrations of different antibiotics were measured by the ultra performance liquid chromatography-tandem triple quadrupole mass spectrometer (ABI 6500, Applied Biology Company, America).

2.2. Analysis of the heavy metals

Fraction procedure of heavy metals: A three-step BCR extraction procedure was applied to extract the heavy metals in the PM, CM and their biochar samples. And the heavy metals were divided into four fractions including F1: acid soluble/exchangeable fraction; F2: reducible fraction; F3: oxidizable fraction and F4: residual fraction, which was described by European Community Bureau of Reference (BCR). The detailed information of BCR extraction procedure can be found in our previous work (Wang et al. 2019a). To obtain the F1-F3, the suspension was centrifuged at centrifugation factor of 3820.2 ($\times g$) for 20 min and then filtered through a 0.22 μm filter. The filtrate was then diluted using HNO_3 (2%) to a constant volume of 50 mL. The obtained filtrate was digested using the mixed acid of H_2O_2/HNO_3 to remove the dissolved organics. The F4 and total content of heavy metals in the PM, CM and biochar samples were determined after digestion using a microwave digestion system with an acid mixture (HNO_3 : $HClO_4$: HF = 5: 5: 2, v/v/v), and then filtrated via the 0.22 μm nylon filter before measurement. Each test was operated three times to keep the data accuracy and the values were presented as mean values $\pm$ standard deviation.

Leaching experiments: The availability and toxicity heavy metals in PM, CM and the biochar samples were impacted by their leachability assessed by the toxicity

characteristic leaching procedure (TCLP) (Xie et al. 2019). For the TCLP, the glacial acetic acid solution with pH of 2.88 was used for extraction with liquid/solid ratio of 20:1. After extraction in the polyethylene tubes and shaken at 200 rpm for 18 hours in a shaking incubator, the supernatant was obtained via centrifugation for digestion with H₂O₂/HNO₃, and then filtrated through 0.22 µm membrane filters for measurement of heavy metals.

Evaluation of risk assessment code: The widely used evaluation of risk assessment code (RAC) was employed to assess the heavy metal toxicity (Leng et al. 2016). The percentage of F1 was used to represent the RAC, which included five degrees: no risk (NR), lower than 1%; low risk (LR), 1-10%; medium risk (MR), 11-30%; high risk (HR), 31-50%; very high risk (VHR), higher than 50% (Zhai et al. 2014).

2.3. Extraction and measurement of the antibiotics

The dried and homogenized samples (0.5 g of raw PM, CM or 1 g of their biochar samples) were added into polytetrafluoroethylene centrifuge tube (50 ml), and 1 mL of the standard solution of 100 µg/L was also spiked. Then the samples were mixed and placed in a refrigerator at 4 °C overnight. After adding 15 mL of extraction solvent (EDTA-McIlvaine buffer: methanol: acetonitrile = 5: 3: 2, v/v/v) and mixing on a vortex mixer at 25 ± 1 °C in the dark for 1 min, all the tubes were ultrasonicated for 15 min and then centrifuged at centrifugation factor of 5000 for 10 min. The obtained supernatant and residue were decanted into a brown glass bottle and extracted with extraction solvent (10 mL) once more, respectively, and the procedure was repeated twice. When the combined supernatants from the three extractions were filtered through a 0.45 µm glass microfiber (GF/F, Whatman), they were diluted to 500 mL using ultrapure water to keep the organic solvent content ≤ 5% in the

solution. More detailed information about the solid phase extraction and purification can be obtained in the literature (Huang et al. 2013). The final obtained samples were stored at 4 °C before measurement. The detailed information of the applied method for all the antibiotics was listed in Table S2. The recoveries for PM, CM and their biochar samples were relevant high, which proved the feasibility of the applied extraction method.

2.4. Laboratory and pilot-scales pyrolysis experiments

All the laboratory-scale pyrolysis experiments were conducted in a fixed bed quartz reactor (Fig. S1a). The pyrolysis temperature varied from 300 to 700 °C. For each experiment, 40 g of PM or CM was inserted into the quartz reactor, and then N₂ (80 mL/min) was introduced for removing the air in the reactor to create an oxygen-free environment. After that, it was prepared as follows: heating the reactor to preset temperatures with heating rate of 15 °C/min; keeping for 45 min; cooling the reactor to room temperature; taking out the biochar from quartz reactor. At last, the obtained biochar was kept in a dryer for further characterization analysis.

For the pilot-scale pyrolysis experiments, it was done in a rotary furnace with 6.0 m in length, 1.5 m in width and 1.5 m in height, and the schematic diagram can be found in Fig. S1b. A screw feeder was applied to feed the PM or CM into the rotary furnace with a treatment capacity of 6 t per day. The rotary furnace was heated by burning wood pellets to keep the temperature at 600 ± 50 °C, and the produced bio-gas/oil was recycled into the chamber and burnt to supply the energy consumed during pyrolysis process. There were three ventilators and thermocouples to supply oxygen for combustion and measure the temperatures, respectively. The retention time for PM or CM in the furnace was about 45 min. The generated biochar was cooled in an oxygen-free environment, and the detailed information about the pilot-scale

pyrolysis process can be found in our previous study (Li et al. 2018a).

3. Results and Discussion

3.1 Effect of pyrolysis temperature on the biochar

3.1.1 Characterization of biochar made from PM and CM

To characterize biochar made from PM and CM at different pyrolysis temperatures, the proximate and ultimate analysis, biochar yield, pH value and specific surface area (S_{BET}) were measured and the results were summarized in Table 1. The biochar yields decreased with the pyrolysis temperature from 300 to 700 °C (50.91 to 35.93% for PM and 52.82 to 36.07% for CM), which resulted from the decomposition of organic matters (Jin et al. 2016). The ash content obviously increased due to the concentrated minerals and loss of organic matters. And the pH presented the opposite trend with the change of biochar yield. It was explained that the alkali salt was released and the acidic surface functional groups decreased during pyrolysis process, causing pH raising from 8.10 to 13.08 for CM (Zheng et al. 2013). In addition, the high pH of biochar samples indicated that it could be used as acid soil amendment. Compared with the S_{BET} of raw PM and CM, improving pyrolysis temperature obviously enhanced the S_{BET} values, such as from 0.08 to 20.91 m²/g for PM, which was resulted from the aggravation of carbonization degree (Jin et al. 2016). In terms of ultimate analysis, all the element contents (except C) decreased with rising pyrolysis temperature due to the continuous decomposition of volatile matters. And the increase trend of C with the pyrolysis temperature was due to the high content of fixed carbon in the raw materials concentrated with decomposition of organic matters during pyrolysis process.

3.1.2 FTIR spectra analysis of PM, CM and their biochars

To further identify the change of chemical functional groups under various

215 pyrolysis temperatures, the FTIR spectra was used to analyze the PM, CM and their
 216 biochars. **Fig. 1** indicates that before pyrolysis, PM and CM showed similar FT-IR
 217 spectra with major peaks at 3405-3443 cm^{-1} , 2923 and 2834 cm^{-1} , 1647 cm^{-1} , 1584
 218 cm^{-1} , 1400-1440 cm^{-1} , 1230 cm^{-1} , and 1060 cm^{-1} , which correspond to $\nu(\text{-OH})$, $\nu_{\text{as}}(\text{-CH}_2)$
 219 CH_2) and $\nu_{\text{s}}(\text{-CH}_2)$, $\nu(\text{-C(O)NH-})$, $\nu(\text{C=C})$, $\delta(\text{-OH})$ and $\delta(\text{CH})$, $\rho(\text{-CH}_2)$, and $\nu(\text{C-OH})$,
 220 respectively (Agrafioti et al. 2013; Li et al. 2018b; Yang et al. 2007; You et al. 2019).
 221 When PM and CM were pyrolyzed at 300 $^{\circ}\text{C}$, all peaks were largely reduced in their
 222 intensities, especially $\nu(\text{-OH})$, $\nu_{\text{as}}(\text{-CH}_2)$, $\nu_{\text{s}}(\text{-CH}_2)$, $\nu(\text{-C(O)NH-})$, $\delta(\text{-OH})$ and $\rho(\text{-CH}_2)$.
 223 Therefore, the phenol, methylene and amides groups were almost eliminated so that
 224 the cellulose structures of PM and CM were transformed into carbonaceous structures
 225 of biochar. In the spectra of PM300 and CM300, typical peaks of biochar can be
 226 identified at 1584 cm^{-1} , 1402 cm^{-1} and 1060 cm^{-1} , which correspond to $\nu(\text{C=C})$, $\delta(\text{CH})$
 227 and $\nu(\text{C-O})$, respectively (You et al. 2019). As the pyrolysis temperature increased to
 228 over 400 $^{\circ}\text{C}$, the $\nu(\text{C=C})$ and $\delta(\text{CH})$ peaks were even more decreased and became
 229 unobvious when the temperature surpassed 600 $^{\circ}\text{C}$. This result indicated that the
 230 aliphatic C-H was converted to CO_2 , CH_4 and other gases or transformed into
 231 aromatic structures with pyrolysis temperature higher than 400 $^{\circ}\text{C}$ (Lu et al. 2013).
 232 The tiny peaks of $\nu_{\text{as}}(\text{-CH}_2)$ and $\nu_{\text{s}}(\text{-CH}_2)$ compared with the much more significant
 233 $\nu(\text{C-O})$ implied that PM and CM were dehydrogenated accompanied by the formation
 234 of C-O-C groups as different forms of oxygen were converted into carbon chains with
 235 carbon-oxygen form (Ho et al. 2017). **The high temperature eliminated most**
 236 **functional groups and transformed part of them into carbonaceous structures, which**
 237 **led to the graphitization of biochar.** This conclusion is supported by the ultimate
 238 analysis in **Table 1**, where the higher temperature decreased the content of H and O
 239 while stabilized the content of C.

3.2 Effect of pyrolysis temperature on heavy metals immobilization

3.2.1 Total concentrations of heavy metals in PM, CM and their biochars

The heavy metals contents in PM, CM and their biochars were important factor for their treatment and application. Thus it was necessary to investigate the immobilization and migration of the heavy metals during pyrolysis process. The total concentrations of heavy metals in PM, CM and their biochars were listed in [Table 2](#). For all the heavy metals, only Zn and Cu presented relative high concentrations of 2739.58 mg/kg vs 2332.27 mg/kg and 610.22 mg/kg vs 741.32 mg/kg in PM and CM, respectively, and the concentration of Zn exceeded its threshold value of 2000.00 mg/kg. It was also reported by other research that the concentrations of Zn and Cu in PM were extremely higher than other kinds of heavy metals, which contributed by the high Zn and Cu concentrations in the food additives for livestock (Meng et al. 2017). In terms of all the heavy metals (except Cd) in biochar samples, they concentrated during pyrolysis, and higher pyrolysis temperature led to higher concentration. It was interpreted by the decomposition of organic matters and lose of volatile matters in the PM and CM. The heavy metals were released during the decomposition process and then co-precipitated with the produced biochar (Wang et al. 2016). Another reason for the higher concentrations of heavy metals in biochar samples was that the lose weight of organic matters was higher than that of heavy metals (Wang et al. 2016). While, the concentration of Cd rose first and then dropped with the increase of pyrolysis temperature. The main reason was that the Cd mainly existed as the form of carbonate and volatilized at higher pyrolysis temperature (Wang et al. 2019b). For PM, although the heavy metals concentrated in the biochar samples, it still did not exceed the threshold values except Zn. While for CM, the concentration of Cu exceeded the threshold value of 1500.00 mg/kg when the pyrolysis temperature was higher than

600 °C with 1545.19 mg/kg. Therefore, the Zn and Cu were the mainly influential heavy metals in livestock and their biochars.

3.2.2 Speciation distributions of heavy metals in PM, CM and their biochars

In fact, the bioavailability and toxicity of heavy metals on the environment were mainly related to their chemical speciation. The chemical speciation assessed by BCR sequential extraction scheme could be divided into four fractions, which lowered in bioavailability and mobilization by $F1 > F2 > F3 > F4$. The speciation distributions of different heavy metals in PM, CM and their biochar samples were presented in Fig. 2.

Zn and Cu were the essential trace elements for livestock and poultry, and their salt compounds were widely applied as food additives for livestock (Lin et al. 2017; Tiquia. 2010). The excess additives cannot be adsorbed efficiently by livestock, resulting in the high concentrations in PM and CM (Table 2). The Zn showed high bioavailability with $F1 + F2$ fractions of 58.09% in PM and 27.60% in CM, respectively. With the pyrolysis temperature increasing from 300 to 700 °C, the proportion of $F1+F2$ fractions declined in their biochar samples (26.75% and 17.10% in biochar samples at 700 °C). Even the fraction of Zn transformed from $F1 + F2$ fractions to $F3 + F4$ fractions, its percentage was still high in the biochar samples. Different from Zn, the $F3$ fraction accounted for the main proportion of Cu in the PM and CM with 96.35% and 68.74%, respectively. As the concentration of Cu in its biochar exceeded the threshold value, its chemical speciation should be paid much attention. With the increase in pyrolysis temperature, the $F3$ fraction converted remarkably into $F4$ fraction. And the $F3 + F4$ fractions reached to 99.09% and 99.44% in the biochar samples obtained at 700 °C, indicating its slight risk on environment. The change was explained by the Cu-organic matter complexes owned high stability, and it was also reported that Cu was mainly existed in organic and

residual phase (Shi et al. 2013). As for Cr, F3 + F4 (mainly F4) occupied large part of the fractions in the PM and CM with 98.19% and 89.77%, then changed to 99.95% and 99.60% at 700 °C, respectively. And the F4 fraction of Pb (only for CM) almost occupied 100% in the biochar obtained even at low pyrolysis temperature of 300 °C.

In terms of Ni, Cd and As, similar with Cr and Pb, their concentrations in their raw manures and biochar samples did not surpass their threshold values of 100.00 mg/kg, 5.00 mg/kg and 300.00 mg/kg at pH < 6.5 (Table 2). While, their bioavailable fractions (F1 + F2) were relevant higher than those of Cr and Pb, so their immobilization performance should be focused on. The F1 + F2 fractions of Ni were 28.55% and 22.06% in PM and CM, and then reduced to 0.89% and 4.00% in the biochar samples at 300 °C respectively, moreover higher pyrolysis temperature had little influence in the proportion. Another obvious change was the decline of F3 fraction and increase of F4 fraction with rising temperature from 300 to 700 °C. The Cd and As presented the same trend with Ni, indicating their well transformation from unstable fractions of F1+F2 to stable fractions of F3+F4.

According to the above results, the F1, F2, F3 and F4 fractions had different distribution for different heavy metals in the PM, CM and their biochar samples. While, the stable fractions of F3 + F4 obviously increased after pyrolysis and higher pyrolysis temperature led to higher percentage.

3.2.3 Leaching characterization and ecological risk assessment

The TCLP method was used to assess the leaching characterization of different heavy metals in PM, CM and their biochars, and the results were listed in Table S3 and Fig. 3. As for raw PM, the leaching concentration of Zn was relevant high with 25.95 mg/L, which exceeded its threshold value of 5.00 mg/L, indicating its high potential environmental risk. The other heavy metals including Cr, Ni, Cd, As and Pb

had low leaching concentrations. After pyrolysis, the leaching concentrations of all the heavy metals reduced and higher pyrolysis temperatures led to lower leaching concentrations. But the concentration of Zn in biochar obtained at 700 °C was 16.36 mg/L, being still higher than the threshold value of 5.00 mg/L. The leaching rates of PM, CM and their biochar samples were presented in Fig. 3. The leaching rates of all the seven heavy metals obviously reduced with pyrolysis temperature. This also verified that the decline toxicity of the leached heavy metals in the biochar samples. Similar to the changes of PM, the pyrolysis technology also presented enhancement effect on the leaching concentrations and leaching rates for CM. The difference was that all the leaching concentrations of the heavy metals in biochar from CM were lower than their threshold values, indicating their low environmental risk.

The risk assessment codes of different heavy metals in PM, CM and their biochars were also summarized in Table 3. The biochar samples performed safer state compared with the raw materials. For the PM, Zn presented high risk, and Ni and As were listed as moderate risk. Other heavy metals were low risk or no risk. After pyrolysis at 700 °C, the risk states of Zn, Ni and As transformed to moderate, no and low risk, respectively, which meant that the risk assessment of the heavy metals was extremely declined. Similar to the change of PM, the risk assessment of all the heavy metals in CM transformed to low risk/no risk after pyrolysis. It was also verified from the pyrolysis of sewage sludge that the heavy metals were well immobilized to decline the risk assessment during pyrolysis process (Jin et al. 2016; Li et al. 2018a). In summary, the pyrolysis presented obvious advantage in heavy metals immobilization during the safe treatment of PM and CM.

3.3 Antibiotics removal during pyrolysis process

3.3.1 Total concentrations of different antibiotics in PM, CM and their biochars

As there were many kinds of antibiotics in livestock feces, so three main classes (macrolides, tetracyclines, sulfonamides) including seven typical antibiotics (TYL, TC, CTC, DOXY, SMZ, SDZ and SMX) were selected to investigate the effect of pyrolysis temperature on the decomposition performance of the antibiotics. The concentrations of the seven antibiotics in the PM, CM and their biochars were presented in Table S4.

Among the seven antibiotics, the concentrations of TC, CTC and DOXY (905.13, 39890.50 and 95500.24 $\mu\text{g/kg}$ in PM vs 3181.13, 46100.34 and 204.95 $\mu\text{g/kg}$ in CM) were extremely higher than those of other antibiotics. Because the TC is the universal antibiotics to enhance the growth of livestock, and the CTC and DOXY are used to prevent livestock from diseases. They were excessively used as additives during feeding livestock. The concentrations of other four antibiotics were relevant low. While, the concentrations of TYL, TC, CTC, DOXY and SDZ remarkably reduced after pyrolysis, and higher pyrolysis temperature resulted in lower concentrations. For TYL, TC, CTC and SMZ, their concentrations decreased to 0 $\mu\text{g/kg}$ (no detected) in the PM and CM biochar samples obtained at 300 °C, indicating their easy decomposition properties. These performances could also be verified from their thermo-gravimetric analysis results (Fig. S2) that all the TYL, TC, CTC and SMZ presented a big weight loss peak near 300 °C. These meant that their structures were obviously changed due to the removal of part functional groups or break of some bonds converting into gases, which led to the loss of weight. In terms of DOXY, SDZ and SMX, their concentrations reduced with pyrolysis temperature increasing to 500 °C (< IQL). But they still needed much higher temperature of 600 °C for the thorough decomposition, indicating their difficult decomposition during pyrolysis process. And it can also be seen from Table S5 that the temperature ranges of weight

loss of these antibiotics were relevant higher. This might explain their higher temperature requirement for completely decomposition. All in all, the pyrolysis technology presented many advantages than other treatment method like composting about antibiotics thorough removal (Pruden et al. 2013). The results indicated that 600 °C was the lowest pyrolysis temperature for completely removing all these antibiotics.

3.4 Pilot-scale verification at optimal pyrolysis condition

After the laboratory investigation, the pyrolysis temperature of 600 °C was selected for pilot-scale verification in a rotary furnace (Li et al. 2018a), confirming the performances of heavy metals immobilization and antibiotics removal in the PM and CM. The pyrolysis temperature was practically controlled at 600 ± 50 °C, and the biochar yields of PM and CM were 35.60% and 36.84%, respectively. The concentrations of heavy metals and antibiotics, heavy metals immobilization and antibiotics removal rate in the biochar were investigated.

Heavy metals immobilization : The total concentrations, risk assessment code and leaching concentrations of all the heavy metals in the biochar samples from pilot-scale tests were also measured (Table 2, Table 3 and Table S3). It can be seen that similar data were obtained from pilot-scale tests compared with those from laboratory-scale experiments at the same pyrolysis condition. A little higher concentrations of all the heavy metals in pilot-scale biochar were caused by the difficulty at controlling exact temperature at 600 °C, sometime the pyrolysis temperature was higher than 600 °C. Meantime, the pilot-scale test using rotary furnace with better heat transfer than laboratory-scale test using fixed bed reactor. The risk assessment codes of the heavy metals in the pilot biochars were also reduced after pyrolysis at 600 °C. And the leaching concentration for all the heavy metals showed

that only Zn exceeded its permissible limit in pilot PM biochar. All the other heavy metals in PM and CM biochars did not pass their threshold values, indicating their low environmental risk.

The speciation distributions of different heavy metals in the pilot biochars were presented in Fig. 4a. Obvious immobilization was completely obtained with conversion from the unstable F1 + F2 fractions to the stable F3 + F4 fractions.

Antibiotics removal: In terms of antibiotics removal performance in the pilot-scale test, the concentrations of seven typical antibiotics in the biochar were measured (Table S4). And their removal rates were presented in Fig. 4b. Similar to the results from laboratory-scale tests, there were no antibiotics detected in the pilot-scale biochar, and all their removal rates reached to 100%. These results also verified that the antibiotics were entirely decomposed during pyrolysis at 600 °C in the pilot-scale tests.

In summary, better performances in the heavy metals immobilization and the antibiotics removal were obtained in the pilot-scale tests. Through the pilot-scale verification, it was proved that the pyrolysis technology presented much advantages in safe treatment and recycle of livestock manures via production of biochar.

4. Conclusions

In this study, PM and CM were converted into biochar through pyrolysis at different temperatures from 300 to 700 °C, focusing on the performance investigations of the heavy metals immobilization and antibiotics removal. The following conclusions were obtained:

(1) The heavy metals in PM and CM were significantly immobilized with converting bio-available fractions to more stable-biological ineffectiveness fractions and the higher pyrolysis temperatures (above 600 °C) favored the heavy metal

immobilization.

(2) The typical antibiotics contained in the PM and CM were greatly removed by pyrolysis process, and they can be completely removed with pyrolysis temperature increasing to 600 °C.

(3) The optimal temperature of 600 °C was selected for pilot-scale verification in a rotary furnace and the similar good results in antibiotics removal and heavy metals immobilization were obtained.

(4) The pyrolysis provided an effective method to immobilize and remove the harmful matters including heavy metals and antibiotics for safe treatment and application of PM and CM.

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