**Reveal a hidden highly toxic substance in biochar to support its effective elimination strategy**

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**ABSTRACT**

With the aim to develop optimized biochar with minimal contaminants, it is important significance to broaden the understanding of biochar. Here, we disclose for the first time, a highly toxic substance (metal cyanide, MCN, such as KCN or NaCN) in biochar. The cyanide ion (CN-) content in biochar can be up to 85870 mg/kg, which is determined by the inherent metal content and type in the biomass with K and Na increasing and Ca, Mg and Fe decreasing its formation. Density functional theory (DFT) analysis shows that unstable alkali oxygen-containing metal salts such as K2CO3 can induce an N rearrangement reaction to produce for example, KOCN. The strong reducing character of the carbon matrix further converts KOCN to KCN, thus resulting biochar with high risk. However, the stable Mg, Ca and Fe salts in biomass cannot induce an N rearrangement reaction due to their high binding energies. We therefore propose that high valent metal chloride salts such as FeCl3 and MgCl2 could be used to inhibit the production of cyanide *via* metal interactive reaction. These findings open a new point of view on the potential risk of biochar and provide a mitigation solution for biochar’s sustainable application.

*Keywords:* *Biochar, Toxic substance, Metal cyanide, Theoretical calculation*

**1. Introduction**

Biochar is globally recognized as a positive contributor to reducing the challenges of soil degradation (through increasing soil nutrient retention) and combating climate change (by carbon sequestration and reducing soil-borne greenhouse gas emissions) (Yue et al., 2019; Chen et al., 2020; Quan et al., 2020). Clearly the composition of the biochar is of vital importance including minimizing toxins (Lu et al., 2018). Previous research has pointed to the potential presence of some problematic substances including polycyclic aromatic hydrocarbons (PAHs) (Keiluweit et al., 2012; Zhao et al., 2020), heavy metals and other elements (such as Cd, Pb, Cu, Zn, and As) (Freddo et al., 2012; Stefaniuk et al., 2016), water dissolved organic matters (WDOMs) (Smith et al., 2016; Ghidotti et al., 2017) and persistent free radicals (Liao et al., 2014; Lieke et al., 2018). Consequently, a series of studies have been performed on the effects of such hazardous chemicals since they can induce biotoxicity inhibiting germination, causing tissue damage and cytotoxicity (Oleszczuk et al., 2013; Sigmund et al., 2017; Hao et al., 2018; Zhang et al., 2019).

Very recently, studies have shown that organic nitrogen and metals can combine and react to form some new N-containing metal substances such as (metal cyanides, MCN) (Tsubouchi et al., 2016; Sevilla et al., 2018; Luo et al., 2019). Metal elements and organic N are commonly found in biomass (Sun et al., 2013; Qiu et al., 2015). Therefore, it can be inferred that biochar can carry this toxic substance (i.e., MCN), especially a biochar produced from a biomass with high content of metals and organic N (i.e., foodwaste, sludge, fungi residues, alga). Its presence or at least the possibility of its presence will have a major negative impact on the perceived value of biochar. Recently, biochar has been one of the reasons shown to have high biotoxicity on plant growth and while this could be due to several possible toxic contaminants (Hameed et al., 2019). Undoubtedly, MCN contamination will reinforce such observations.

Clearly an effective MCN controlling strategy is vital to support the sustainable application of biochar and the method must be applicable to a wide range of potential biochar feedstocks, such as agricultural straw, biogas residue, drug residues, livestock manure, and food waste (Zhang et al., 2014a; Opatokun et al., 2015; Zhang et al., 2015; Wang et al., 2017). Biomass are normally rich in various types of metal elements (such as K, Na, Ca, Mg and Fe) and can have different levels of N contents. Currently, there are a series of knowledge gap on MCN formation during the production of biochar, for example, (1) whether various inherent metals of biomass will exhibit synergistic or antagonistic effects on MCN formation, (2) whether the anion of the biomass inherent metal will affect the MCN formation, (3) whether the growth of MCN in a biochar can be inhibited by the antagonistic effect of some metals. These questions need to be addressed if we can continue to see biochar as an environmental asset.

Herein, and with the overall aim of developing a method to inhibit the formation of MCN in biochar, we have first developed a prediction model for its formation on the basis of original biomass characteristics. Secondly, MCN formation mechanisms in biochar are systematically considered by both experimental and theoretical calculation methods. Thirdly, some constraints on biochar production methods are adopted so as to inhibit MCN formation. In this way, we can indeed achieve sustainable-biochar without the presence of MCN.

**2. Materials and methods**

*2.1. Natural biomass and preparation of biochar*

18 types of biomass were collected from various industries of China and listed at Supplementary Table S1 in details. These collected samples were freeze dried, then the raw materials were crushed and sieved through a 40-mesh sieve. Biochar samples were prepared *via* slow pyrolysis reaction under nitrogen gas (N2) flow of 100 mL/min at 800 °C (heating rate of 5 °C/min) for 1 h in a box-type resistance furnace (OFT-1200X, HF-Kejing Co., Ltd., Anhui). The yield of the biochar samples was recorded, and the biochar samples were stored in vacuum-sealed bags for further use. The mental elements of biomass are detected by ICP-OES (5100/G8481A, Agilent, USA) after HNO3-HClO4-HF digestion.

To investigate the MCN formation mechanisms in biochar, plant protein (wheat protein) with low ash content (< 1.0 %) was used as a basic N-containing biomass (12.4 %). While K2CO3, Na2CO3, CaCO3, MgC2O4, FeC2O4, KCl, K2HPO4, and K2SO4 were simulated as inherent metal salts in biomass. The weight ratio of different metal salts and biomass was 1/10. Specially, the weight ratio of K2CO3 to biomass were further displayed at 0, 1/20, 1/10, and 1/5. The mixture of plant protein and inherent metal salt was shaken in aqueous solution for 24 h, and then freeze-dried and heated up to 500 °C - 900 °C for 1 h under a 100 mL/min N2 flow. The yield of the biochar samples was recorded, and the samples were stored in vacuum-sealed bags for further use. Finally, to remove any inorganic salts, the selected samples were thoroughly washed with HCl (2 M) and distilled water in a fume hood, then dried in an oven at 100 °C overnight and filtered through a 100-mesh sieve. For the inhibition study of MCN, MgCl2 and FeCl3 were acted as inhibitor with the weight ratio to biomass is 0, 1/500, 1/50, 1/5.

*2.2. Characteristic of materials*

The CHNS analysis of the washed samples was performed using an elemental analyzer (Vario EL III, Elementar, Germany). The crystal structures of samples (unwashed) were determined by X’Pert PRO powder X-ray diffraction (XRD, Rigaku Ultimate IV, Japan) equipped with Cu Kα radiation between 2*θ* ranges of 10 – 80 °. The surface area and porosity of the washed biochar were determined by nitrogen adsorption/desorption at -196 °C using a Autosorb iQ2 instrument (Quantachrome, USA) after degassed at 300 °C for 6 h. The surface area (*S*BET) and total pore volume (*V*T) were determined by the Brunauer-Emmett-Teller (BET) equation. Pore size distribution was calculated with the Density Function Theory (DFT) model.

The pyrolysis CO gas released in the sample’s pyrolysis process was determined by on-line mass spectrometry (MS, Hiden QIC-20, UK). Before MS analysis of CO, pyrolysis oil was removed by tetrahydrofuran solution in solid CO2 bath. The carrier gas and m/z value for CO gas analysis was Ar and 28, respectively. CN- content in solution was quantitatively analyzed using an ion chromatograph (Dionex ICS-600, USA) with Abe detector. The liquid solution was collected by the biochar samples soaked in NaOH solution (0.1 mol/L) with ultrasonic dispersion for 30 mins at 25 °C. Specially, the CN- content in samples with Ca, Mg, Fe are extracted based on the GB5085.3-2007. The supernatant was then filtered using a 0.45 μm nylon membrane filter for further analysis.

*2.3. Absorption of bisphenol A*

To examine the changes of biochar adsorption ability, bisphenol A (BPA) is chosen as target contaminant due to it is high frequently detected in surface water and its potential toxicity to the environment. BPA adsorption isotherms were achieved in the concentration of 2 - 100 mg/L with 50 mg/L biochar at 25 °C. After the adsorption equilibrium (16 h), the supernatant was followed by filtration using a 0.45 μm polytetrafluoroethylene (PTFE) membrane filter for analysis of BPA concentration. The concentration of BPA was measured by UV/Vis spectrometer (TU-1901, Pgeneral, Beijing, China) at 280 nm absorbance. *Langmuir* model was used to fit the adsorption isotherms.

*2.4. Characterization of bio-oil samples*

The molecular composition of bio-oil (collected in HPLC methanol) was analyzed by the ESI FT-ICR MS (Bruker Apex ultra, Bruker, Germany) with a 9.4 T superconducting magnet. The operating conditions for negative ion formation were conducted as our previous study (Zhu et al., 2017). The mass range was set to m/z 200-800. In order to enhance the signal-to-noise ratio and dynamic range, all of 128 scan FT-ICR data sets were accumulated. Methodologies for FT-ICR MS mass calibration, data acquisition, and processing have been described before (Liu et al., 2010). Scans of methanol were performed as base-line to ensure that it was clean of the instrument before analyzing the samples.

*2.5. Theoretical calculation details*

All calculations were carried out using Gaussian 6.0 program. Density functional theory (DFT) computational method was used to optimize the equilibrium geometries of the reactants, intermediates, transition states, and products. In the calculations, a geometry optimization and frequency calculation are performed first at the B3LYP/6-31g\* level and then a subsequent frequency analysis is carried out at the B3LYP/def2svp level, also obtained an overall energy barrier. Intrinsic reaction coordinate (IRC) calculations were performed to ensure the correctness of each transition state.

**3. Results and discussion**

*3.1. MCN content in actual biomass derived biochar*

Many common types of biomass such as sawdust, wheat straw and livestock manure show only small amounts of cyanide ion (CN-) in the resulting biochar. However, food waste derived biochar (40286 mg/kg), phycocyanin derived biochar (85870 mg/kg) and corn protein (with K2CO3)derived biochar (23251 mg/kg) have significant CN- contents (Supplementary Table S1). This can be correlated with the presence of abundant N and K and Na content. Thus, CN- content in biochar may significant effected by biomass characteristics.

Fig. 1a displays the relationship between biomass characteristics and CN- content in the associated biochar using regression analysis to describe the possible conditions associated with the production of MCN. The color bars represent the intensity of the R value (multi-correlation coefficient), and a strong linear correlation is found between Na content and CN- content, indicating that Na is one dominating factor on MCN formation. Na and CN- content in 18 samples were further evaluated and it can be seen that the R2 value is 0.63 after linear fitting (Fig. 1b). The red band is the 95 % confidence interval for linear fitting (black solid line). It can be observed that, several dots are outside of the red band (tag with a triangle). Some of the dots (No.1 and 2, are cow dung and biogas residue) are associated with biomass samples which are rich in Na content but result in low CN- content. Both of these samples share a similar characteristic, which is abundance in Ca and Fe in the biomass. This may imply that these two metals have a negative effect on the formation of MCN during the biochar formation process. Another, a dot (No.3, corn protein with K2CO3) corresponds to limited Na content but with high CN- content; this is because this sample contains a large amount of K. From these results it can be inferred that, in comparison to Ca, Mg and Fe, the presence of alkali metals (such as K and Na) in biomass may provide sites to support CN- formation, an inference supported by the Pearson correlation between the released CN- and the metal content of biomass (Fig. 1c). It should be pointed out that K content has not exhibited strong correlation with CN- content in this diagram. This observation may be explained by the fact that abundant K-containing samples are limited in studied samples, thus it couldn’t observe obvious positive tendency between K and CN- content.

Lastly, the forecast model of CN- content in biochar calculated and based on the characteristics of biomass precursor is analyzed in a four-dimensional slice plot (Fig. 1d). K content, Na content and the sum of Ca, Mg, Fe content in biomass are the independent variables *x*, *y* and *z*, while the dependent variable (*v*) is the CN- content in the biochar (intensity of the color in the cube). The regression analysis equation is calculated as following:

*v* = 288.18 *x* +1977.38 *y* -341.22 *z* + 561.24 (1)

This equation exhibits a good regression coefficient, R2=0.87. It can be concluded that the charring process of biomass can produce MCN in a process that is enhanced by alkali metals (K and Na) but limited by Ca, Mg, and Fe. We must therefore be wary of biomass with abundant alkali metal (such as food waste and marine) as raw material for biochar production.

Additionally, with the background that biochar industry is in a rapidly development supported by China government, more than 30% waste biomass in annual year will be applied in biochar manufacturing (Wu et al., 2019). In these 18 types biomass samples, corn straw (259 million tons per year, 2017) and fungi residue (92 million tons per year, 2017) are common biomass in China for biochar production. Based on above analysis, their biochar can associate certain amount of MCN (105 mg/kg for corn straw derived biochar and 251 mg/kg for fungi residue derived biochar, respectively). In such circumstances, if 30 % (percentage of production in annual year in China) corn straw or fungi residue is used to biochar production, considerable CN- content can be generated as a by-product, as shown in Supplementary Fig. S1. As can be clearly note that, these generated CN- content will increase the potential environment risk, especially in its production process, environment application and soil carrier.

*3.2. MCN production mechanism in biochar*

As shown in Fig. 2a, the CN- contents in biochar derived from biomass (plant protein) with Na2CO3, K2CO3 and K2SO4 are 6972 mg/kg, 19116 mg/kg and 2555 mg/kg, respectively. Typically, biomass with unstable O-containing alkali salts, such as alkali carbonate (such as Na2CO3 or K2CO3) and alkali metal sulphates (such as K2SO4) exhibit strong combination ability with organic nitrogen in biomass to yield MOCN and then to MCN though carbothermal reduction (MOCN + C → MCN + CO). Results strongly suggest that the metal salt present in the biomass plays an important role in MCN formation. It seems that metals with higher valence (such as Ca, Mg and Fe) in biomass are less likely to form MCN in the derived biochar, confirmed by the measured CN- content in biochar and the corresponding XRD pattern (Fig. 2a and Supplementary Fig. S2a). This failure is believed due to the precursor MOCN not being formed in the biochar because organic N is not well coordinated by such metals. These results agree well with the CN- forecasting model (Fig. 1d).

The formation curves of CO in peak 1 (KOCN + C → KCN + CO) further confirms that KCN can be produced in biochar derived from biomass containing K2SO4 and K2CO3 (Supplementary Fig. S2b and c). In contrast, K2HPO4 restricts KCN formation attributing that ionized K+ is firstly to complex with metaphosphate radical to form a stable substance with cyclical structure (KPO3), as indicated by corresponded XRD spectrum (Supplementary Fig. S2b). KCl also blocks KCN formation since oxygen atoms are needed for the formation of the critical intermediate KOCN. This mechanism will be further analyzed by density functional theory method (DFT).

For depth study, K2CO3 is further used as specific inherent metal salt of biomass to study the mechanism of MCN production. As show in Fig. 2a, the CN- content in biochar increases with pyrolysis temperature (from 500 to 800 °C), illustrating that the heating temperature can facilitate the carbothermal reduction reaction. The distinct peak in the XRD (especially 2*θ* = 28°) of KCN in XRD also increases with increasing pyrolysis temperature (Supplementary Fig. S3a) although it rapidly decreases after 900 °C due to its volatilization (Fig. 2a). Increasing the K2CO3 content in biomass also increases the CN- content in biochar (Fig. 2a), as suggested by the stronger intensity of KCN in the XRD spectra (Fig. 2b). Thus, enhancement of the CO in peak 1 induced by KOCN reduction (KOCN + C → KCN + CO) further increased (Fig. 2c). In summary, MOCN from complexation reaction between O-containing metal salt and organic N is the key precursor to support MCN formation.

It also should be noted that this reaction consumes both carbon matrix and organic N, thus simultaneously reducing the yield of biochar and its N content though boosting the BET surface area of the biochar (after washing) (Fig. 2d and e). The strongly positive correlation (R2=0.89) between the yield of CO in peak 1 and the BET surface area of biochar samples confirms that CO from carbothermal reduction reaction is the main pore-foaming factor (Fig. 2e). Therefore, the changes in the biochar resulting from the formation of MCN, including an improvement of micropore structure (Supplementary Fig. 3b), that can lead to the biochar having improved adsorption properties of organic pollutant (Borchardt et al., 2017). Three samples with different BET surface areas were selected for bisphenol A (BPA) absorption due to its potential toxicity to the environment and highly detection frequency in surface water (Chen et al., 2016; Wang et al., 2016). The samples are named *A-x*, where *x* indicates the different samples (Supplementary Table S2). As can clearly be seen from Supplementary Fig. S3c, *A-3* sample exhibits excellent pollutant removal which can primarily be attributed to its improved porous structure.

*3.3. Mechanism of MCN formation calculated by DFT (density functional theory) method*

As studied above, the requirement condition for KCN formation in biochar is the complexation reaction between O-containing unstable K salt and organic N to form KOCN. Therefore, DFT has been used to gain a deeper insight into the production mechanism of KOCN. We first focused on the energy pathway for the decomposition of pyrrole to HCN, pyrrole being a common N-containing pyrolysis species (Tian et al., 2014; Zhang et al., 2014b). According to analysis of the bio-oil (Fig. 3a), compounds with DBE=5 and 6 are associated to pyrrole-N or pyridine-N compounds. The intensity of these compounds in the N2 spectrum is significantly decreased for biomass containing K2CO3 (Fig. 3b). The results imply that HCN can be released from the decomposition of pyrrole-N and pyridine-N and the HCN can provide CN- for KOCN formation (Chen et al., 2018). HCN is selected as a typical example with CN- containing compound from pyrolysis product of biomass for K2CO3 complexation.

According to the calculation, after the internal hydrogen transfer and ring-opening of pyrrole, one of the possible pathways of HCN formation is illustrated in detail in Supplementary Fig. S4a, b. We then looked at the formation route of KOCN *via* reforming of K2CO3 and HCN at high temperature. The energy barriers of the main reaction steps are shown in Fig. 4a-c for two scenarios. In pathway one (Fig. 4a), CO32- first complexes with two HCN molecules to form a 7-membered heterocyclic compound, then in the presence of K+, hydrogen migration reaction and dehydrogenation reaction occur. Simultaneously, ring-opening of polycyclic compound is induced to further produce two OCN-s. Differing from pathway one, pathway two firstly involves complexation with HCN, and an oxygen from CO32- is reacted with HCN to form KOCN (Fig. 4b). With K+, the hydrogen bond is broken to generate OCN-. Another HCN is complexed to produce a new compound (Fig. 4b, IM3). After that, reorganization of the structure produces a new OCN-. Comparison of the two paths for OCN- production shows the energy barriers of transition states in pathway one is much higher than in pathway two; meanwhile, from the reactants to the products, the energy barriers are -44.92 kJ/mol and -169.55 kJ/mol, respectively, indicating that pathway two is more favorable to OCN- formation. The detail of energies and relative energies of various compounds of respective states shows in Table S3 and Table S4. We believe that the optimal pathway is mainly attributed to absence of ring formation so that it proceeds *via* a very low energy transition state. Therefore, it can be concluded that O-containing alkali salts play an important role in KOCN formation; it can also be indirectly proven that biomass with KCl cannot complex with organic N to form KOCN.

Additionally, the effects of Na+, Ca2+ and Mg2+ on OCN- formation have been determined in Fig. 4c, the energy barriers from IM1 to IM7 are -147.39 kJ/mol, 425.71 kJ/mol and 537.51 kJ/mol respectively. It was found that Ca2+ and Mg2+ lead to the higher energy products, in contrast with K+ and Na+ in Fig. 4d. This may be attributed the hard Lewis acidity of Na+ and K+, which are good for open-loop reaction and hydrogen migration (Li, 1993). Also, when the C-O is broken, they can stabilize products such as OCN- and H2 (Khampuang et al., 2015). Thus, within this work, the theoretically proposed pathways on OCN- formation support the mechanism of MCN production. These conclusions will play an important role in achieving a comprehensive understanding of the OCN- and further MCN formation during biomass charring.

*3.4.* *Inhibition mechanism of MCN during biomass pyrolysis*

MCN has been fully recognized to be a highly toxic substance (Manar et al., 2011; Choi et al., 2012; Lee et al., 2015), thus, it urgently requires effective method to mitigate MCN content in biochar. As above discussed, the inhibition of MCN can be achieved though the blocking of MOCN formation, because MOCN is sole precursor of MCN. In addition, it has been well documented that the oxygen atom from metal salts is important for forming OCN-, and KCl cannot react with organic N to form KOCN. Therefore, if K2CO3 and metal chloride salt (e.g. MgCl2, FeCl3) in biomass can lead to a reaction to form a thermally stable product such as KCl via metal recombination reaction, thus, KCN in biochar can be completely inhibited due to lack of a precursor (KOCN) (Fig. 5a). As the results show in Fig. 5b, MgCl2 and FeCl3 can well act as inhibitors to prevent the production of MCN. When the addition of FeCl3 is increased to 1/50 (the weight ratio between FeCl3 and biomass), CN- content is reduced to 0 mg/kg. The XRD pattern of biochar samples shows that, KCN is completely inhibited and only KCl and Fe2O3 can be observed at this mass ration (insert Fig. 5b and Fig. 5c), a possible equation can be considered as follow:

3K2CO3 + 2FeCl3 → 6KCl + Fe2O3 + 3CO2↑ (2)

KCl and Fe2O3 are stable compounds and cannot easily form KOCN. Similar principles can be applied to the reaction between K2CO3 and MgCl2, when only KCl and MgO can be detected in the XRD pattern (Fig. 5c).

Additionally, a successful application has been demonstrated in food waste (actual waste biomass) derived biochar, and NaCN formation is completely inhibited after FeCl3 treatment (Fig. 5d). It is also worth noting that NaCl and Fe2O3 can be observed in the XRD pattern instead of NaCN (insert of Fig. 5d). Therefore, it is believed that high valence metallic chlorides, such as FeCl3 and MgCl2, are efficient inhibitors to prevent MCN production during biochar manufacturing, an extremely important conclusion for a rapidly growing industry producing biochar (Zhu et al., 2016; Gou et al., 2019).

**4. Conclusions**

Alkali metals (such as Na and K) in biomass can induce the production of MCN in biochar. However, Fe, Mg and Ca in biomass show antagonism with alkali metals during pyrolysis and their presence inhibits MCN formation in biochar. Importantly, unstable O-containing alkali salts in biomass (such as K2CO3 and Na2CO3) tend to complex with organic N to produce MOCN. In turn, MOCN undergoes carbothermal reduction with the carbon matrix and produces MCN. This process can promote the performance of biochar but severely limits its application especially as an environmental remediator. To control the formation of cyanide, we have proven a highly efficient and low-cost technology simply involving metal chloride salts to completely inhibit CN- formation in biochar. Thus, we can envisage a way to deal with the potentially highly disrupting formation of toxic cyanide in otherwise very useful biochar.

**Conflicts of interest**

There are no conflicts to declare.

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**Appendix A. Supplementary data**

Supplementary data associated with this article can be found online.

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