Effect of porous corncob on the removal of HCN in cigarette mainstream smoke

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Abstract

In order to reduce the hydrogen cyanide (HCN) release in cigarette mainstream smoke, a new type of porous corncob (PCC) material which was different from traditional corncob-based activated carbon was prepared by a two-step chemical reaction of carboxymethylation and cupric ion complexation. Fourier Transformation Infrared Spectroscopy (FTIR) showed that the carboxymethyl group had been introduced onto the corncob, the carboxymethyl content and the cupric ion loading amount were measured. The x-ray photoelectron spectrometer (XPS) results showed that the Cu content on the surface of PCC was much higher than that of the whole material. The scanning electron microscope (SEM) and nitrogen adsorption-desorption results suggested that PCC had a porous structure. With the increase of the amounts of chloroacetic acid and sodium hydroxide in carboxymethylation reaction and the concentration of cupric ion aqueous solution in complexing reaction, the BET surface areas and pore volumes increased, while the most probable pore sizes of PCCs were close to each other. Compared with the control cigarette, the addition of PCC could effectively remove the HCN release in cigarette mainstream smoke, and the highest reduction rates of HCN per total particulate matter (TPM) was 72.4 %.

1. Introduction

Hydrogen cyanide (HCN) is a highly toxic substance that can be absorbed through the mucous membranes and eyes, and it is a very active inhibitor of several human respiratory enzymes. The toxic mechanism of HCN is mainly as follows: the cyanide ion combines with the ferric iron in cytochrome oxidase, which blocks the electron transfer of ferric iron in the oxidation, finally, the tissue cells cannot use oxygen and form internal asphyxia [1–4]. As an important industrial compound, HCN is widely used in many fields, such as nylon production, ore extraction, electroplating, printing and so on. At the same time, it also occurs naturally, although its abundance is very low. Many plants such as bitter almond, apple core, bamboo shoot, cassava and so on contain cyanogenic glycoside which can release HCN when the plants are grated, chewed or otherwise. In addition, the exhaled air of human beings contains trace amounts of HCN. Moreover, the smoke, especially from the combustion of nitrogenous materials such as PU and so on, contains plentiful HCN [5–7]. Meanwhile, HCN is also present in the cigarette smoke, which is recognized as a harmful component in cigarette smoke and has been included in several lists concerning harmful components in cigarette smoke. It is also one of the representative harmful components in cigarette mainstream smoke [8–11]. The HCN release in cigarette mainstream smoke is approximately 3–200 μg/cigarette (cig) [12]. HCN is distributed in both the gas phase and particle phase, and the gas/particle ratio was close to 1:1. The HCN in cigarette smoke is mainly produced by the oxidative decomposition of nitrogen-containing compounds during the combustion process of tobacco. And the proteins and amino acids in tobacco are the main precursors of HCN [9, 11, 13–16]. HCN in cigarette smoke is a major cilia toxic substance, which may have a harmful effect on health, especially the central nervous system.
Therefore, it is of significance to study the methods of reducing the HCN release in cigarette mainstream smoke to improve the safety of cigarette products and protect the health of smokers.

At present, the main method to reduce the HCN release in cigarette mainstream smoke is to add adsorbent materials to the cigarette filter. For example, Caraway JW et al prepared a cigarette filter containing a porous resin composed of chitosan derivatives such as chitosan cross-linked with glutaraldehyde or glyoxal. Chitosan derivatives were used to selectively filter cigarette smoke, especially to remove aldehydes, HCN, heavy metals and carbonyl compounds [20]. McCormack A et al added activated carbon impregnated with transition metals to the filter. In contrast to the activated carbon used in standard cigarette filters, this modified activated carbon could effectively remove HCN in cigarette smoke [21]. Hou HW et al synthesized lamellar γ-AlOOH architectures successfully by hydrothermal route using hexadecyl trimethyl ammonium bromide as a structure-directing agent and precipitating agent. The material could effectively remove the HCN in toxic pollutant solution and cigarette smoke [22]. Guo L et al prepared modified starches and investigated their effect on the adsorption of the composition from cigarette mainstream smoke. Cross-linked phosphorylated porous starch was found to be useful to adsorb ammonia, crotonaldehyde and HCN from cigarette mainstream smoke [23].

Zhe W et al used the hydrothermal method to synthesize a metal-organic framework porous material of copper-1, 3, 5-benzenetricarboxylic acid (II) (Cu-BTC) which had a large specific surface area and good thermal stability. Cu-BTC could reduce the release of HCN from cigarette mainstream smoke selectively and had no obvious effect on the release of conventional smoke components from cigarette mainstream smoke [24]. Sun P et al prepared functional porous carboxymethyl cellulose/cellulose acetate composite microspheres by double emulsion-solvent evaporation method, which could effectively remove the HCN in cigarette smoke [25]. In addition, many other research results suggested that ion exchange resin, molecular sieve, amine-transition metal complex, titane nanotube, berberine and so on also have some certain effect on the removal of HCN in cigarette smoke [26–30]. But so far, there is a lack of adsorption materials that can really be applied to cigarettes on a large scale to reduce HCN release in cigarette smoke, which may be related to the performance of HCN adsorption, cost, safety of the adsorbent materials and so on. Therefore, it is still very attractive for researchers to find new adsorption materials with good performance.

Corncob is a very common crop byproduct, and it has the advantages of high yield, low price and so on. The main components of corncob are cellulose, hemicellulose and lignin, and the hydroxyl group in the molecular structure shows some certain reactivity which is convenient for chemical modification [31–36]. At present, the research on the corncob-based porous materials was basically focused on the corncob activated carbon whose preparation generally requires two steps of high temperature carbonization and activation [37, 38]. However, in this study, cheap corncob was selected as the raw material and a new type of porous corncob (PCC) material was obtained under relatively mild, simple and green reaction conditions which was different from traditional activated carbon derived from corncob. Specifically, based on the structural characteristics of corncob, the hydroxyl group in the molecular structure of corncob was used as the reaction active site to carry out the two-step chemical reaction of carboxymethylation and cupric ion complexation, and then PCC was obtained. Meanwhile, the influence of preparation parameters on PCC was studied. Finally, PCC was applied to cigarette, and its effect on the HCN removal in cigarette mainstream smoke was investigated.

2. Materials and methods

2.1. Materials

The corncob (CC) came from a farmland near Zhengzhou, and the following treatments should be carried out before use: First, the bran layer on the surface of CC and the cotton layer inside CC should be removed, and then the remaining intermediate layer was crushed and sieved to collect the 40–80 mesh granules, the CC granules were finally obtained after drying at 65 °C under vacuum for 24 h.

Absolute ethanol and chloroacetic acid were analytical reagents and purchased from Beijing Chemical Works, Beijing, China. Hydrochloric acid was analytical reagent and purchased from Luoyang Chemical reagent factory, Luoyang, China. Sodium hydroxide and copper sulfate pentahydrate were analytical reagents and purchased from Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China.

2.2. Methods

2.2.1. Preparation of PCC

(1) Carboxymethyl corncob (CMCC) preparation

6 g sodium hydroxide was added to 120 ml ethanol solution (90 vol. %) and stirred until dissolved. 5 g CC and 6 g chloroacetic acid were then added in turn. The mixture was heated to 60 °C for 3 h and then cooled.
to room temperature. After that, they were adjusted to neutral using hydrochloric acid and filtrated, the filter cake was dried at 65 °C under vacuum for 24 h and CMCC was obtained in the end.

(2) PCC preparation
5 g CMCC was added to 100 ml of 0.15 mol l\(^{-1}\) copper sulfate aqueous solution, which was stirred for 4 h at room temperature and then filtrated. The filter cake was rinsed with deionized water until the filter liquor became colorless. After that, the filter cake was added into 100 ml of absolute ethanol and stirred to wash for 1 h at room temperature. After filtrating, the filter cake was rinsed with 50 ml of absolute ethanol and dried at 65 °C under vacuum for 24 h, PCC was finally obtained.

2.2.2. Characterization
The materials were characterized by Fourier Transformation Infrared Spectroscopy (FTIR, Thermo Nicolet, USA). The CMCC carboxymethyl content was determined based on the GB 1886.232–2016 of Chinese national standards [39]. The cupric ion loading amount of CMCC was measured by 7500 inductively coupled plasma mass spectrometry (ICP-MS, Agilent, CA, USA) [25]. The surface element composition of the materials was analyzed by x-ray photoelectron spectrometer (XPS, ESCALAB 250Xi, ThermoFisher). Microtopography of the materials was characterized using JSM-7500F scanning electron microscope (SEM, JEOL, Japan). Nitrogen adsorption-desorption measurements were carried out by a Tristar II 3020 gas sorptometer (Micromeritics, GA, USA), the standard Brunauer-Emmet-Teller (BET) method was used to calculate the surface area and the Barrett-Joyner-Halenda (BJH) method was used to analyze the pore structure [25].

2.2.3. Evaluation of PCC for the HCN removal in cigarette mainstream smoke
According to the method in our previous work [25, 40], the effect of PCC on the HCN removal in cigarette mainstream smoke was evaluated by the device which was used to simulate the addition of absorbents to the cigarette filter, and the material amount added was 30 mg cig\(^{-1}\) [41].

3. Results and discussion

3.1. Preparation and characterization of PCC
PCC was prepared by a two-step chemical reaction of carboxymethylation and cupric ion complexing using CC as the raw material. The FTIR spectrum (figure 1) showed that the absorption at 1605 cm\(^{-1}\) was attributed to the carbonyl group vibrations of CMCC which meant the carboxymethyl group was introduced onto CC, and the absorption at 1599 cm\(^{-1}\) was attributed to the carbonyl group vibrations of PCC. The carbonyl group vibrations of PCC showed a red shift compared to CMCC, which was due to the complexation of carboxymethyl groups in PCC with cupric ions [42].

Table 1 showed that the carboxymethyl content of CMCC was 2.31 mmol g\(^{-1}\) and the cupric ion loading amount of PCC was 0.90 mmol g\(^{-1}\).

Table 2 showed the XPS analysis results of the materials. It could be seen that the surfaces of CC and CMCC materials both mainly contain C and O and there was no Cu. The O/C ratio of CMCC was higher than that of CC, which was mainly attributed to the carboxymethyl of CMCC. The surface of PCC material mainly contains C, O and a small amount of Cu. The atomic concentration of Cu was 3.14%, corresponding to a molality of 0.90 mmol g\(^{-1}\), which was higher than the data (0.90 mmol g\(^{-1}\)) measured using ICP-MS presented in table 1. The results indicated that the Cu content on the surface of PCC was much higher than that of the whole material, which meant that Cu might mainly distribute on the surface of PCC. Therefore, these characterization results demonstrated the presence of carboxymethyl group and cupric ion on the surface of PCC, as well as the complexation of them. In addition, the O/C ratio of PCC was higher than that of CMCC, which might be due to the fact that parts of the PCC substrate surface were covered by the pores formed after the complexation of carboxymethyl with cupric ion.

Figure 2 showed the SEM results of the materials. It could be observed that there were no obvious pores on the surface of CC (figure 2(a)) and CMCC (figure 2(b)), while many pores could be observed on the surface of PCC (figure 2(c)) and the pores were nanoscales (figure 2(d)). The nanopores observed on the surface of PCC were formed after the complexation of carboxymethyl with cupric ion, the reason was that CMCC who had strong hydrophilic carboxymethyl groups exhibited a swollen state in water, while the complex formed after the complexing reaction of carboxymethyl with cupric ion and exhibited an insoluble state, and then the nanopores were formed, which was a bit similar to the pore formation principle of MOFs [43–45].
Figure 3(a) was the nitrogen adsorption-desorption isothermal curves of the materials. It could be seen that the adsorption-desorption isothermal curves of CC and CMCC were similar to each other, and with the change of relative pressure, the quantities adsorbed were basically unchanged. But the adsorption-desorption isothermal curve of PCC was obviously different from that of CC and CMCC, the quantity adsorbed of PCC varied with the change of relative pressure. Figure 3(b) gave the pore size distribution of PCC, the most probable pore size of PCC was 28.92 nm which indicated PCC had a mesoporous structure.

Table 1. Functional groups contents in the materials.

| Sample | Carboxymethyl content (mmol g⁻¹) | Cupric ion loading amount (mmol g⁻¹) |
|--------|---------------------------------|-------------------------------------|
| CMCC   | 2.31                            | /                                   |
| PCC    | /                               | 0.90                                |

Table 2. The atomic concentration and O/C ratio of the materials obtained by XPS analysis.

| Sample | Atomic (%) | O/C  |
|--------|------------|------|
| CC     | 74.39      | 25.61| 0.34  |
| CMCC   | 66.07      | 33.93| 0.51  |
| PCC    | 55.22      | 41.64| 3.14  | 0.75  |

Figure 1. FTIR of CC (a), CMCC (b), and PCC (c).

Figure 2. SEM images of CC (a), CMCC (b) and PCC (c), (d).
Table 3 provided the nitrogen adsorption-desorption experimental data of the materials. The BET surface area, pore volume and most probable pore size of CC and CMCC were detected without any data which meant that there were no obvious pores on the two materials. The BET surface area, pore volume and most probable pore size of PCC were 35.01 m$^2$ g$^{-1}$, 0.17 cm$^3$ g$^{-1}$ and 28.92 nm respectively, which were consistent with the SEM results.

### Table 3. Nitrogen adsorption-desorption experimental data of the materials.

| Sample  | BET surface area (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Most probable pore size (nm) |
|---------|----------------------------------|-------------------------------|-----------------------------|
| CC      | —                               | —                            | —                           |
| CMCC    | —                               | —                            | —                           |
| PCC     | 35.01                           | 0.17                          | 28.92                       |

Figure 3. (a) Nitrogen adsorption-desorption isothermal curves of the materials. (b) The pore size distribution of PCC.

Table 4. Influence of the preparation parameters on the materials.

| Preparation parameters | Characterization of materials |
|------------------------|-------------------------------|
| Sample | Chloroacetic acid amount (g) | Sodium hydroxide amount (g) | Carboxymethyl content (mmol g$^{-1}$) | Cupric ion loading amount (mmol g$^{-1}$) | BET surface area (m$^2$ g$^{-1}$) | Pore volume (cm$^3$ g$^{-1}$) | Most probable pore size (nm) |
|---------|-------------------------------|-----------------------------|--------------------------------|--------------------------------|-------------------------------|-------------------------------|-------------------------------|
| A1      | 3.0                           | 3.0                         | 1.22                          | 0.48                          | 19.17                         | 0.10                          | 30.73                         |
| A2      | 6.0                           | 6.0                         | 2.31                          | 0.90                          | 35.01                         | 0.17                          | 28.92                         |
| A3      | 9.0                           | 9.0                         | 2.89                          | 1.13                          | 42.30                         | 0.19                          | 29.23                         |
| A4      | 12.0                          | 12.0                        | 3.11                          | 1.25                          | 44.20                         | 0.19                          | 29.12                         |

Table 3 provided the nitrogen adsorption-desorption experimental data of the materials. The BET surface area, pore volume and most probable pore size of CC and CMCC were detected without any data which meant that there were no obvious pores on the two materials. The BET surface area, pore volume and most probable pore size of PCC were 35.01 m$^2$ g$^{-1}$, 0.17 cm$^3$ g$^{-1}$ and 28.92 nm respectively, which were consistent with the SEM results.

### 3.2. Influence of preparation parameters on PCC

In order to investigate the effect of preparation conditions on PCC, several major parameters were performed by varying the amounts of chloroacetic acid and sodium hydroxide in carboxymethylation reaction and the concentration of cupric ion aqueous solution in complexing reaction.

#### 3.2.1. The amounts of chloroacetic acid and sodium hydroxide

As presented in table 4, the influence of the amounts of chloroacetic acid and sodium hydroxide in carboxymethylation reaction on the materials was investigated with the other preparation conditions unchanged, and the nitrogen adsorption-desorption isothermal curves of the materials were presented in figure 4.

As could be seen from table 4, from A1 to A4, with the increase of the amounts of chloroacetic acid and sodium hydroxide, the carboxymethyl contents and cupric ion loading amounts both increased. The results might be explained by the fact that with the amounts of chloroacetic acid and sodium hydroxide increased, more
hydroxyl groups were replaced and thus the carboxymethyl contents increased, so that more cupric ions could react with carboxymethyl groups and the loading amounts of cupric ion increased gradually.

In addition, as seen from table 4 and figure 4, the adsorption-desorption isothermal curves of A1 to A4 were similar to each other, the BET surface areas and pore volumes of A1 to A4 showed an increasing trend. The possible explanation for this was that with the increase of the carboxymethyl contents of A1 to A4, more pores were formed after the complexing reaction of carboxymethyl group with cupric ion. Meanwhile, the most probable pore sizes of A1 to A4 were all about 30 nm, this might be due to the fact that the complexing reaction of carboxymethyl groups with cupric ions was uniform, resulting in the similar pore size.

3.2.2. The concentration of cupric ion aqueous solution
As provided in table 5, the influence of the concentration of cupric ion aqueous solution on the materials was investigated with other preparation conditions unchanged, and the nitrogen adsorption-desorption isothermal curves of the materials were presented in figure 5.

The data in table 5 revealed that the loading amounts of cupric ion of B1 to B4 increased with the increase of the concentration of cupric ion aqueous solution. This was due to the fact that the complexing reaction of carboxymethyl with cupric ion became more sufficient with the concentration of cupric ion aqueous solution increased, resulting in the increase of the cupric ion loading amounts.

Furthermore, as set out in table 5 and figure 5, the adsorption-desorption isothermal curves of B1 to B4 were similar to each other, and the BET surface areas and pore volumes of B1 to B4 showed an increasing trend. The reason might be that more pores were formed after the complexing reaction between carboxymethyl group and cupric ion with the increase of the concentration of cupric ion aqueous solution of B1 to B4. Meanwhile, the most probable pore sizes of B1 to B4 were all about 30 nm, the possible explanation was that the complexing reaction of carboxymethyl groups with cupric ions was uniform, resulting in the similar pore size.

3.3. Evaluation of PCC for the HCN removal in cigarette mainstream smoke
The results of HCN removal in cigarette smoke were given as table 6. Compared with the control cigarette, the TPM release of all the test cigarettes decreased slightly, while the HCN release decreased significantly. Combined with the data in tables 4 and 5, from A1 to A4, with the increase of the BET surface areas and the cupric ion loading amounts, the HCN reduction rates per TPM which had more meaningful reference index increased, up
to 72.4%. From B1 to B4, the HCN reduction rates per TPM increased with the increase of the BET surface areas and the cupric ion loading amounts, and the highest was 68.2%.

PCC could effectively remove the HCN in cigarette mainstream smoke should be the results of physical adsorption and chemical adsorption. The porous structure of PCC expanded the contact area between PCC and the HCN, and it was beneficial to the physical adsorption between PCC and HCN. Furthermore, PCC material contains cupric ions, the stability constant $\log \beta$ of cupric ion and acetic acid was 3.2, which was much lower than that of cupric ion and cyanide ion ($\log \beta = 27.3$) [46]. Therefore, the complexing reaction between PCC and cyanide ion could occur, and HCN could be chemically adsorbed.

In addition, as shown in tables 3 to 5, the BET surface area and the cupric ion loading amount of PCC had an important influence on its ability to remove HCN. There were many methods to improve the BET surface area and cupric ion loading amount of the materials, such as the use of new materials, new technologies and so on [47–51]. In this study, the BET surface area and the cupric ion loading amount increased simultaneously by increasing the amounts of chloroacetic acid and sodium hydroxide in carboxymethylation reaction or the concentration of cupric ion aqueous solution in complexing reaction. And the physical adsorption and chemical adsorption were enhanced with the increase of the BET surface area and the cupric ion loading amount, resulting in the improvement of the adsorption capacity of PCC for HCN.

**Table 6.** The HCN removal in cigarette mainstream smoke.

| Sample | Total particulate matter (TPM) (mg/cig) | TPM reduction rate (%) | Hydrogen cyanide (HCN) release (μg/cig) | HCN reduction rate (%) | HCN reduction rate per TPM (%) |
|--------|----------------------------------------|------------------------|----------------------------------------|------------------------|--------------------------------|
| Control | 13.6 | — | 114.5 | — | — |
| A1     | 13.0 | 4.4 | 47.0 | 59.0 | 57.1 |
| A2     | 13.1 | 3.7 | 35.6 | 68.9 | 67.7 |
| A3     | 13.2 | 2.9 | 31.3 | 72.7 | 71.8 |
| A4     | 13.2 | 2.9 | 30.7 | 73.2 | 72.4 |
| B1     | 12.9 | 5.1 | 48.6 | 57.6 | 55.3 |
| B2     | 13.0 | 4.4 | 37.4 | 67.3 | 65.8 |
| B3     | 13.1 | 3.7 | 35.6 | 68.9 | 67.7 |
| B4     | 13.2 | 2.9 | 35.3 | 69.2 | 68.2 |

Note: HCN reduction rate per TPM = (HCN release of control sample/TPM of control sample - HCN release of test sample/TPM of test sample)/(HCN release of control sample/TPM of control sample).

**Figure 5.** (a) Nitrogen adsorption-desorption isothermal curves of the materials. (b) The pore size distributions of the materials.

**4. Conclusions**

(1) A new type of PCC material was prepared by carboxymethylation reaction and cupric ion complexing reaction in this study, which was completely different from the traditional activated carbon based on corncob. The BET surface area and pore volume of PCC could be adjusted by varying the preparation parameters, while the most probable pore sizes of PCCs were close to each other.

(2) PCC could significantly remove the HCN release in cigarette mainstream smoke, and the HCN reduction rates per TPM could reach up to 72.4%, which meant that PCC had a great potential application as an...
adsorbent of HCN in cigarette mainstream smoke. At the same time, it also provided a new reference for the reuse of corncob.

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