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Functional materials development from Kitchen waste

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Abstract

Value-added hybrid materials can be produced by using KW as raw material. It was found that the morphologies of the hybrid carbon materials derived from KW presented similar structure with those made by pure saccharides, and mainly depended on the valence state of the iron. Both the cations (Fe(III), Fe(II)) and the anions (Cl-, SO42-, NO3-) of the iron salts significantly affected the reaction pathway of organic compounds and the retention of the nutrients in the KW. The products developed in this study are applicable for adsorption and catalysis in environmental and catalytic fields.

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1. Introduction

In recent years, bioconversion of Kitchen waste (KW) into valuable materials was widely investigated, including fermentation for biogas, ethanol production, vermicompost for organic fertilizer [4,5], etc. However, bioconversion methods are generally time consuming and have strict requirements for precursors. Furthermore, the high content of moisture, lipid, salts and pathogens in the garbage should be unfavorable for biochemical treatment or as feedstuff directly. In contrast, thermochemical methods, such as pyrolysis, gasification, combustion and hydrothermal liquefaction [3] are much more efficient and rapid for reduction and disinfection of KW, but usually with relative higher treatment costs and some complexities in process management. Amongst various techniques, hydrothermal carbonization (HTC) process is a promising candidate for small-scale, decentralized applications for waste streams with high moisture content, and synthesis of novel carbon-based materials with a wide variety of potential applications.

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The purposes of this preliminary research is to (1) investigate the feasibility of using KW for hybrid carbon materials production; (2) identify the effects of different iron salts on the characteristics of the solid products.

2. Experimental

Raw KW was collected from a college restaurant. Experiments were carried out in stainless steel autoclaves. The morphology and size of the products were observed by employing a transmission electron microscope (TEM), performed on a Hitachi H-800 transmission electron microscope (Tokyo, Japan) at an accelerating voltage of 200 kV. The surface morphology and elements were studied by scanning electron microscope-energy dispersive X-ray spectra (SEM-EDX, HITACHI S-3000N, Japan). Powder X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation.

3. Results and discussion

3.1. Morphology of the solid products

After HTC treatment, KW became massive amorphous particles due to its macromolecular biological structures (images not shown). However, various nanostructures were formed after iron salts addition, as shown in the SEM (a, d) and TEM (b-c, e-f) images of Fig. 1. The morphologies of the solid products were mainly affected by the cations of the iron salts. Besides of the irregular particles (Fig. 1a), hollow carbon spheres ranging from nano to micron can be obtained in the presence of ferrous ions (Fig. 1b-c).

![Fig. 1. SEM (a,d) and TEM (b,c,e,f) images of various solid products with addition of ferrous (a-c) and ferric salts (d-e).](image-url)
3.2. Effects of different iron salts on the carbonaceous materials

Char yield is defined as the mass ratio of demineralized solid product to dried biomass. Fig. 2 shows the effect of various iron salts on the char yield and ash content after HTC process. It can be seen that the maximum char yield and ash content were obtained by ferric nitrate addition, sulphates addition caused the next-maximum char yield and ash content, then the chlorides. Ferric salts had higher char yields but lower ash content compared to ferrous salts. In a word, both the valence state of the iron and counter anions had big influences on the char yield and ash content of the solid products. It is presumed that ferric ion which acts as a Lewis acid could catalyze the dehydration of the saccharides forming a higher yield of HMF. While the generation of HMF from the precursor is the key prerequisite step for the carbonization reaction and production of carbonaceous materials.

![Graph showing char yield and pH values](image)

Fig. 2. Effects of different iron salts on (a) char yields and pH values prior to HTC, (b) ash contents and pH values after HTC. 
(3, 2 = Fe$^{3+}$, Fe$^{2+}$; N, S, C = NO$_3^-$, SO$_4^{2-}$, Cl$^-$)

As shown in Fig. 2, the pH values of the system prior to (pHinitial) and after (pHfinal) the HTC process varied with the addition of different iron salts. Due to the stronger hydrolysis of ferric ions, a significant decrease of the initial pH value from 7 to around 2 can be observed, other than 5 with ferrous ions addition. It is known that acidic system at the initial stage of HTC process is favorable for catalysis and hydrolysis and carbonization of the carbohydrates thus leading to higher char yields [5]. It also has been reported that in a pH range from 3 to 7, the rate of reaction is largely independent of H$^+$ and OH$^-$ concentration, probably because the hydrogen bond between cellobiose and water is stronger at high temperatures than the influence of pH in this region [6], and that might be the main reason for the difference in the char yields with ferric and ferrous salts addition. On the other hand, the final system pH value plays crucial role in the ash content of the solid product, more iron compounds could deposit in the system with higher pH values (Fig. 2b).
Fig. 3. Effects of various iron salts on the atomic H/C, O/C, N/C ratios of the KW and various chars. (3, 2 = Fe3+, Fe2+; N, S, C = NO3-, SO42-, Cl-)

The HTC process might involve dehydration, condensation, and decarboxylation reactions, resulting in a loss of some carbon, hydrogen, and oxygen. Van Krevelen diagrams were used for delineating different reaction pathways of HTC of KW with different iron salts. As illustrated in Fig. 3 the dotted line represents the dehydration reaction pathway for KW. It can be seen that the conversions of KW are predominantly governed by dehydration process, especially with addition of ferric nitrate. While a shift above the dotted line suggests that decarboxylation also occurs when the system without additives or with addition of ferrous salts. Ferric chloride and sulphate addition resulted in significant decreases of the atomic H/C and N/C ratio of the char products (shown in Fig. 3b). These results indicate that deamination might occur during these systems.

4. Conclusions

This study developed a novel process for KW recycle. In the process addition of ferric salts greatly reduced the initial pH value of the system which catalyzed hydrolysis, carbonization and deamination of KW, thus leading to massive carbon microsphere yields and decreased the nitrogen content in the solid products, while ferrous salt promoted decarboxylation and resulted in lower char yields.

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