

Walnut shell modified by maleic anhydride: synthesis and characterization

ABSTRACT

A novel modified walnut shell (MWNS) was prepared by the reaction between maleic anhydride and raw walnut shell (WNS) in ethyl acetate. MWNSs with different carboxyl values (MWNS1 and MWNS2) are obtained and characterized by Fourier transform infrared (FTIR). The effects of reaction temperature, reaction time and maleic anhydride concentration on the carboxyl value of MWNS have been investigated. The results show that the carboxyl value of MWNS increases with the increase of temperature and the concentration of maleic anhydride, and it increases with the increase of reaction time until the equilibrium reached. When the reaction temperature is 77 °C, reaction time is 180 min and maleic anhydride concentration is 2.0 mol/L, the carboxyl value of MWNS is up to 2.80 mmol/g.

Keywords: modified walnut shell; synthesis; characterization; carboxyl value.

Comment [N1]: The word 'increase' is repeated 4 times in 3 lines successively and some verbs are in present and other in the past.

Comment [N2]: Succession of information on the temperature, the time of the reaction, the concentration of maleic anhydride and the concentration of the carboxylic acid groups without showing why the production of carboxylic acid group is important what will be the future applications of this novel product?

Comment [N3]: carboxylic acid groups and not 'carboxyl'

1 INTRODUCTION

China is a traditional agricultural country, producing a large amount of agricultural and forestry wastes every year. Most of these wastes are mainly treated by incineration, which not only causes serious environmental pollution, but also causes serious waste of resources. Various agricultural and forestry wastes such as walnut shell [1], peanut husk [2], sugarcane bagasse [3], rice husk [4], wheat residue [5] and sawdust [6] are lignocellulosic residues, and characterized by low cost, widely available, biodegradable, resource recycling and environment-friendly [7]. Currently, only a part of the agricultural and forestry wastes is utilized in several industries, such as processing fodder, making compost, producing fermented products and compacting composite materials [8]. Thence, it is important to consider how to use these resources more efficiently.

Walnut shell (WNS) mainly composed of cellulose (~17.7%), hemicelluloses (~36.1%) and lignin (~36.9%) [9], which contain many functional groups and could react with other groups (e.g., carboxyl, epoxy and amine groups) [10,11] to synthesize new materials as packings or adsorbents. It can be used as a substitute for adsorbent materials mainly due to its nontoxicity, high mechanical strength and chemical stability. However, untreated WNS has low metal adsorption capacity. Much work has been done to increase the adsorption capacity of WNS by reacting with fatty acid [10], acrylic acid [12], epichlorohydrin and diethylenetriamine [11] and so on. Our laboratory has synthesized a maleic anhydride modified walnut shell [13] which was

used to adsorb metal ions. However, the current work mainly focuses on the adsorption capacity of modified walnut shells, and little research on the modification process. Therefore, it is necessary to study the effects of different reaction conditions on the carboxyl value of modified walnut shells and find better reaction conditions to synthesize products with higher carboxyl value.

In this study, modified walnut shell (MWNS) was prepared by reaction of maleic anhydride with WNS in ethyl acetate. The effects of reaction temperature (T), reaction time (t) and maleic anhydride concentration (C_{MAH}) on the carboxyl value (C_{COOH}) have been evaluated, and MWNSs with different carboxyl values (MWNS1 and MWNS2) are obtained. WNS, MWNS1 and MWNS2 are characterized by Fourier transform infrared (FTIR).

Comment [N4]: the temperature of the reaction and not reaction temperature

Comment [N5]: time of reaction instead of reaction time

Comment [N6]: carboxylic acid groups instead of carboxyl

2 EXPERIMENTAL

2.1 Reagents

The chemicals involved in this study were maleic anhydride (MAH), ethyl acetate (supplied by Shanghai Westlong Biochemical Technology Co. Ltd.), sodium hydroxide, hydrochloric acid (35 wt%) (purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd.) and anhydrous ethanol (obtained from Shanghai Titan Scientific Co., Ltd). All of them were of AR grade. WNS were obtained from market. Prior to the reaction, the powder of WNS was swollen in deionized water and dried, and then sieved to obtain the particles with diameter range of 100-200 mesh.

2.2 Preparation of MWNS

The synthesis process of MWNS was as follow: first, the dried WNS was soaked into anhydrous ethanol for 30 min at room temperature and filtered. Then a certain amount of MAH is added to a 250mL three-necked flask containing ethyl acetate to obtain different concentrations of MAH solution (C_{MAH}), and WNS obtained in the first step is added. The mixture was heated to a set reaction temperature (T) and the reaction was performed for certain period of time(t). Subsequently the solid material was filtered, washed with deionized water until the eluent pH reached almost neutral. Finally, the washed particles were dried in oven to a constant mass.

The above operation processes were duplicated at different reaction time (15 min, 30 min, 45 min, 60 min, 90 min, 120 min, 150 min, 180 min, 210 min, 240 min and 270 min) with different MAH concentrations (0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L and 3.0 mol/L) at different reaction temperatures (25 °C, 45 °C, 65 °C and 77 °C), and the corresponding MWNS products can be obtained.

The associated reaction of the modification process was showed in Fig. 1.

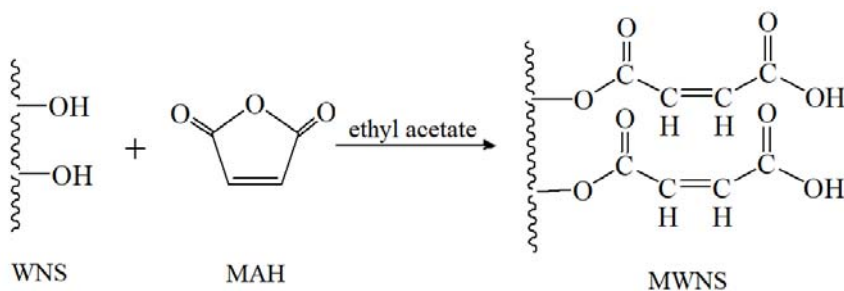


Fig. 1. The associated reaction of the modification process

2.3 Determination of Carboxyl Value

Comment [N7]: under reflux system ? make a precision

Comment [N8]: the quantity must be clearly defined

Comment [N9]: 'were obtained' instead of 'can be obtained'.

The carboxyl value of MWNS was measured by acid-base titration. MWNS was soaked into NaOH solution for over two days. The leaving NaOH was analyzed by back-titration with HCl solution. The carboxyl value(C_{COOH}) was calculated as

$$C_{\text{COOH}} = \frac{C_{\text{NaOH}} V_{\text{NaOH}} - C_{\text{HCl}} V_{\text{HCl}}}{w} \quad (1)$$

where $w(\text{g})$ is the mass of MWNS. C_{NaOH} , $C_{\text{HCl}}(\text{mol/L})$ are the concentrations of NaOH and HCl. V_{NaOH} , $V_{\text{HCl}}(\text{L})$ are the volumes of NaOH and HCl.

3 RESULTS AND DISCUSSION

3.1 Characterization of WNS, MWNS1 and MWNS2

The reaction between MAH and WNS involves formation of a chemical bond between C-O-C group of MAH and the -OH group from WNS. The interaction leads to the formation of -COO- group, and also introduce the -COOH group. Three samples (WNS, MWNS1($C_{\text{COOH}} = 1.35 \text{ mmol/g}$) and MWNS2 ($C_{\text{COOH}} = 2.39 \text{ mmol/g}$)) were characterized by Fourier transform infrared (FTIR) (NicoletMQGNA-IR 550, Thermo Electron Corp., USA) adopting KBr technique. The results are shown in Fig. 2. From Fig. 2, it can be confirmed by the appearance of the new IR absorption bands at 1749 cm^{-1} and 1655 cm^{-1} , corresponding to carboxyl group and *cis* C=C bond, respectively. Besides, the higher the carboxyl value, the more obvious the band at 1749 cm^{-1} . So we can conclude that MAH is successfully grafted onto the WNS surface.

Comment [N10]: Carboxylate groups -COO- are characterized in FTIR by to bands 1545 and 1454 cm^{-1} that are not mentioned in the FTIR part so why the author speaks about these groups.

Comment [N11]: Carboxyl acid groups

Comment [N12]: The band of 1749 cm^{-1} remains to the free carboxylic groups but according to the Fig1 , we expected dimeric acid acid intra-association between the carboxylic acid groups that might appeared at 1700 cm^{-1} 1690 cm^{-1} .

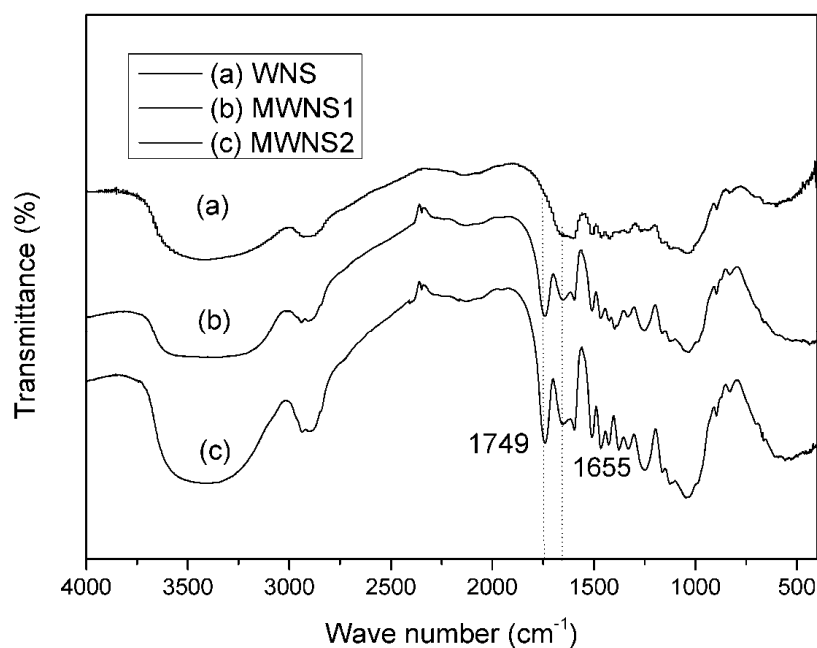


Fig.2. FTIR spectra of (a) WNS, (b) MWNS1 and (c) MWNS2.

3.2 Effect of reaction temperature and reaction time

The chemical reaction is generally affected by the reaction temperature [14]. The effects of reaction temperature and reaction time on carboxyl value of MWNS were investigated at the maleic anhydride concentration 3.0 mol/L. The reaction temperature and time varied from 25 °C to 77 °C (the boiling point of ethyl acetate), and 0 to 270 min, respectively. The results are shown in Fig. 3. From Fig. 3, the carboxyl value of MWNS increases with the increase of temperature at the same moment, and at a constant temperature it increases with increasing in reaction time up to a relative stable value at which point the modification reaction reaches to equilibrium. Table 1 lists the values of time when the reaction reaches to equilibrium (t_{eq}) and equilibrium carboxyl values

Comment [N13]: By the time of the reaction instead of reaction time.

(C_{COOH}^{eq}) at different temperatures. From Table 1, t_{eq} decreases from 240 min to 150 min, and C_{COOH}^{eq} increases from 1.94 mmol/g (at 25 °C) to 2.92 mmol/g (at 77 °C) when the temperature rises, indicating the reaction rate and the equilibrium carboxyl values increase as the temperature increases. This is because the increase in temperature promotes molecular motion and increases the possibility of molecular collisions. On the other hand, since the modification reaction is a solid-liquid reaction which may be controlled by the internal diffusion. With the increase in temperature, diffusion coefficient of MAH in WNS increases. Therefore, the reaction temperature is preferably controlled at the boiling point of solvent (77 °C).

Comment [N14]: Increase cited 4 times in 3 consecutives lines

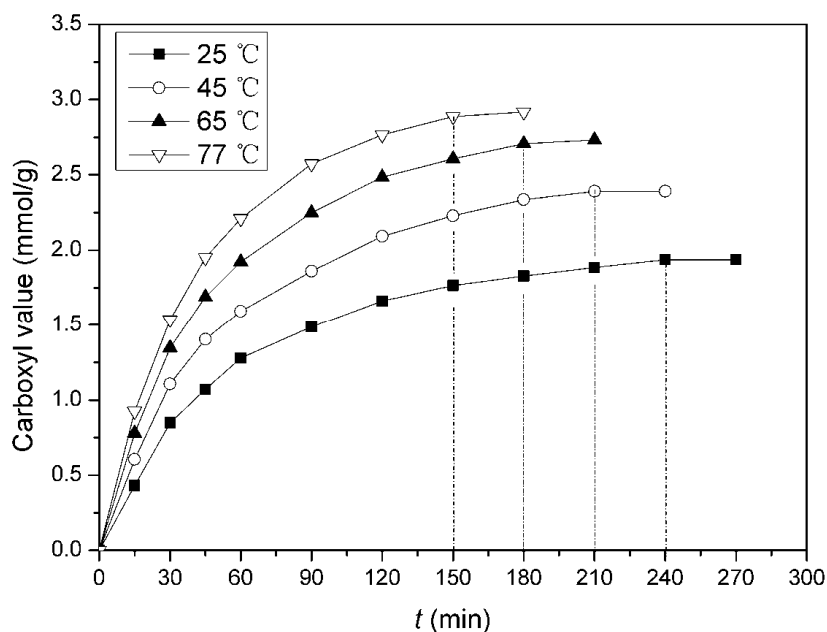


Fig. 3. Effect of reaction temperature and reaction time on carboxyl value of MWNS.

Table 1. Reaction time to be equilibrium and equilibrium carboxyl values of MWNS at different

temperatures

$T (^{\circ})$	25	45	65	77
$t_{eq} \text{ (min)}$	240	210	180	150
$C_{COOH}^{eq} \text{ (mmol/g)}$	1.94	2.39	2.73	2.92

3.3 Effect of the concentration of maleic anhydride

Concentration of maleic anhydride is another important factor affecting the carboxyl value of MWNS. The effect of the concentration of maleic anhydride was investigated by varying C_{MAH} from 0.5 mol/L to 3.0 mol/L at 77 $^{\circ}$. These results are shown in Fig. 4. From Fig. 4, at the same moment, the carboxyl value of MWNS increases with the increase of the concentration of maleic anhydride. This may be due to an increase in the concentration gradient between the maleic anhydride solution bulk and the surface of WNS. When C_{MAH} is less than 2.0 mol/L, the constant carboxyl value increases with the increase of C_{MAH} , but it only has a slight increase when C_{MAH} is larger than 2.0 mol/L. For example, at 180 min, the carboxyl value increases from 1.93 mmol/g to 2.80 mmol/g and from 2.80 mmol/g to 2.92 mmol/g when the value of C_{MAH} changes from 0.5 to 2.0 mol/L and from 2.0 to 3.0 mol/L, respectively. Thus, the suitable concentration of maleic anhydride is 2.0 mol/L due to its economy.

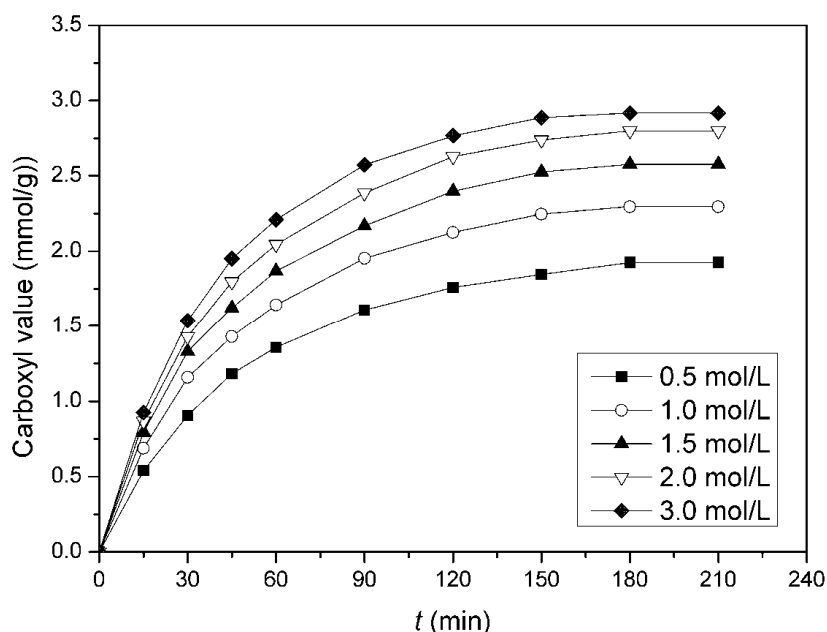


Fig.4. Effect of the concentration of maleic anhydride on carboxyl value of MWNS.

4. CONCLUSION

A novel modified walnut shell (MWNS) was prepared by reacting maleic anhydride with raw walnut shell (WNS) in ethyl acetate. MWNSs with different carboxyl values (MWNS1 and MWNS2) are obtained and characterized by Fourier transform infrared (FTIR). The effects of reaction temperature, reaction time and maleic anhydride concentration (C_{MAH}) on the carboxyl value of MWNS have been evaluated. The results show that at a constant temperature the carboxyl value of MWNS increases with the increase of reaction time, and remains a relatively stable value (C_{COOH}^{eq}) at the moment the modification reaction reaches to equilibrium (t_{eq}). When the temperature increases

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from 25 °C to 77 °C, t_{eq} reduces from 240 min to 150 min and C_{COOH}^{eq} of MWNS increases from 1.94 mmol/g to 2.92 mmol/g. In addition, C_{COOH}^{eq} of MWNS at 180 min increases from 1.94 mmol/g to 2.80 mmol/g when C_{MAH} is increased from 0.5 mol/L to 2.0 mol/L, and it changes a little when C_{MAH} is larger than 2.0 mol/L.

Comment [N16]: the equilibrium temperature t_{eq}

Comment [N17]: the verb must be in the past. Add the optimal conditions by citing the optimal temperature, time of reaction concentration of maleic anhydride that can lead to the highest level of carboxylic acid groups in the modified product.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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