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Walnut Shell Modified by Maleic Anhydride: Synthesis and Characterisation

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Authors' contributions

This work was carried out in collaboration between all authors. Author SL designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors ZZ and WX managed the analyses of the study. Author SL managed the literature searches. All authors read and approved the final manuscript.

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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 carboxylic acid groups values (MWNS1 and MWNS2) are obtained and characterised by Fourier transform infrared (FTIR). The effects of reaction temperature, reaction time and maleic anhydride concentration on the carboxylic acid groups value of MWNS have been investigated. The results show that the carboxylic acid groups value of MWNS is positively correlated with the temperature of the reaction and the concentration of maleic anhydride, and it increases with the increase of reaction time until the equilibrium was reached. When the reaction temperature is 77℃, the reaction time is 180 min, and maleic anhydride concentration is 2.0 mol/L, the carboxylic acid groups value of MWNS is up to 2.80 mmol/g. The obtained product has a higher adsorption capacity for metal ions (e.g., Pb^{2+}, Ni^{2+}) and can be used in the wastewater treatment.

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Keywords: Modified walnut shell; synthesis; characterisation; carboxylic acid groups value.

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 utilised 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., carboxylic acid, epoxy and amine groups) [10,11] to synthesize new materials as packaging or adsorbents. It can be used as a substitute for adsorbent materials mainly due to its nontoxicity, high mechanical strength and chemical stability [11]. 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]. Our laboratory has synthesised 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 find the best conditions that enhance the carboxylic acid groups production.

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

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 was obtained from the market. Prior to the reaction, the powder of WNS was swollen in deionised water and dried, and then sieved to obtain the particles with a diameter range of 100-200 mesh.

2.2 Preparation of MWNS

The synthesis experiments of MWNS were carried out in a 250 mL three-necked flask containing a condenser, thermometer and mechanical stirrer, and a short description of experiment was as follow: first, the dried WNS was soaked into anhydrous ethanol for 30 min at room temperature and filtered. Then a quantity of MAH (~3.0 g) is added to a 250 mL 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 a time noted (t). Subsequently, the solid material was filtered, washed with deionised water until the eluent reached neutral pH. Finally, the washed particles were dried in the oven until the mass of the product remains constant.

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℃, 45℃, 65℃ and 77℃), and the corresponding MWNS products were obtained.

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

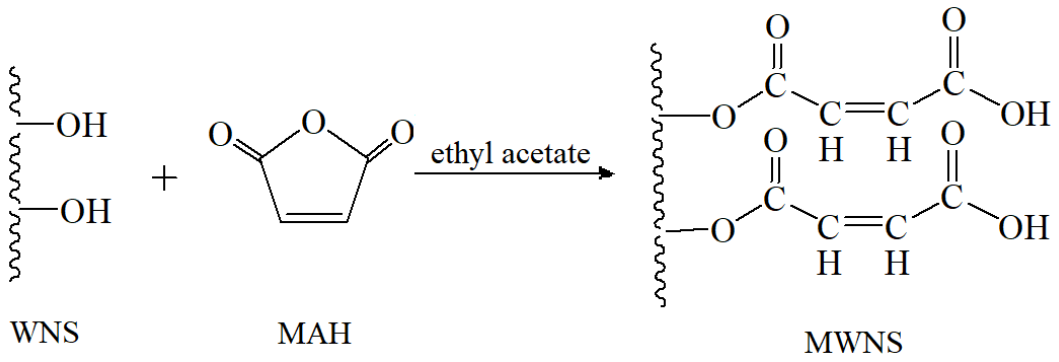

Fig. 1. The associated reaction of the modification process

2.3 Determination of Carboxylic Acid Groups Value

The carboxylic acid groups 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 carboxylic acid groups value(C_{COOH}) was calculated as

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

where w(g) is the mass of MWNS. C_{NaOH}, C_{HCl} (mol/L) are the concentrations of NaOH and HCl. V_{NaOH}, V_{HCl}(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 the formation of a chemical bond between the 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 carboxylic acid groups (-COOH). Three samples (WNS, MWNS1(C_{COOH} =1.35 mmol/g) and MWNS2 (C_{COOH} =2.39 mmol/g)) were characterised by Fourier transform infrared (FTIR) (Nicolet MQGNA-IR 550, Thermo Electron Corp., USA) adopting KBr technique. The corresponding FTIR spectra were represented in Fig. 2. Fig. 2 showed to band at 1583 cm^{-1} and 1463 cm^{-1} related to carboxylate groups, and it can be confirmed by the appearance of the new IR absorption bands at 1749 cm^{-1} and 1655 cm^{-1}, corresponding to the carboxyl group and *cis* C=C bond, respectively. So we can conclude that MAH is successfully grafted onto the WNS surface.

3.2 Effect of Reaction Temperature and Reaction Time

The chemical reaction is generally affected by the temperature of reaction [14]. The effects of the temperature and the time of reaction on carboxylic acid groups value of MWNS were investigated at the maleic anhydride concentration 3.0 mol/L. The reaction temperature and time varied from 25℃ to 77℃ (the boiling point of ethyl acetate), and 0 to 270 min, respectively. The results are shown in Fig. 3. From Fig. 3, the carboxylic acid groups value of MWNS increases with the increase of temperature at the same moment, and at a constant temperature, it increased with increase in the reaction time up to a relatively stable value at which point the modification reaction reaches the equilibrium. Table 1 lists the values of time when the reaction reaches the equilibrium (t_{eq}) and equilibrium carboxylic acid groups value (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℃) to 2.92 mmol/g (at 77℃) when the temperature rises, indicating the reaction rate and the equilibrium carboxylic acid groups values are positively correlated with the temperature. 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, the diffusion coefficient of MAH in WNS increases. Therefore, the reaction temperature is preferably controlled at the boiling point of the solvent (77℃).

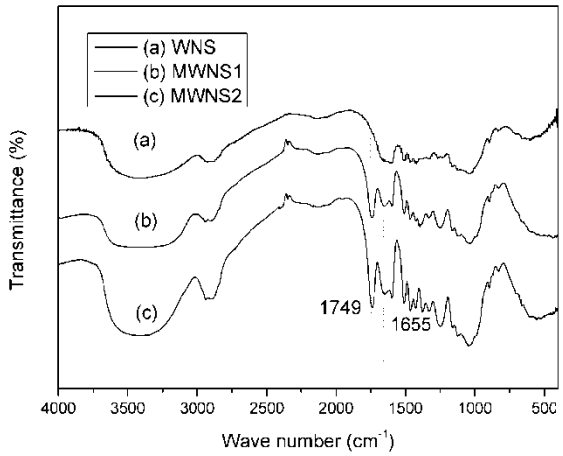

Fig. 2. FTIR spectra of (a) WNS, (b) MWNS1 and (c) MWNS2

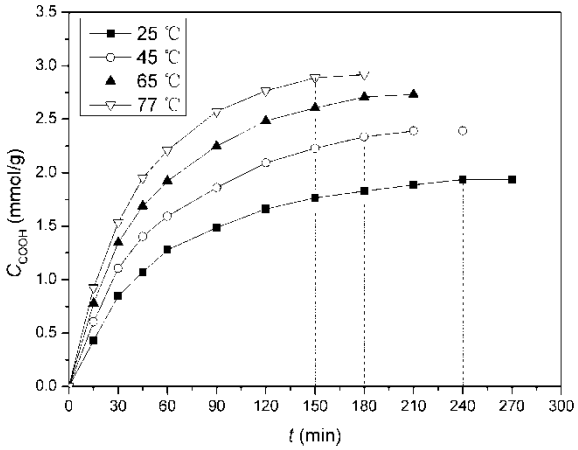

Fig. 3. Effect of reaction temperature and reaction time on carboxylic acid groups value of MWNS

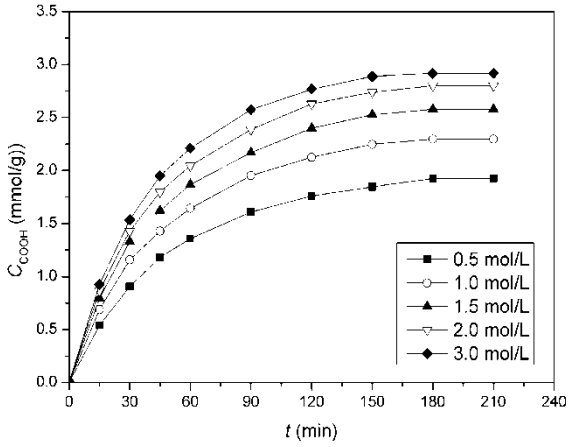

Fig. 4. Effect of the concentration of maleic anhydride on carboxylic acid groups value of MWNS

Table 1. Reaction time to be equilibrium and equilibrium carboxylic acid groups values of MWNS at different temperatures

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

3.3 Effect of the Concentration of Maleic Anhydride

The concentration of maleic anhydride is another important factor affecting the carboxylic acid groups 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℃. These results are shown in Fig. 4. From Fig. 4, at the same moment, the carboxylic acid groups 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 in the bulk and the surface of WNS. When C_{MAH} is less than 2.0 mol/L, the constant carboxylic acid groups 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 carboxylic acid groups 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.

4. CONCLUSION

A novel modified walnut shell (MWNS) was prepared by reacting maleic anhydride with the raw walnut shell (WNS) in ethyl acetate. MWNSs with different carboxylic acid groups values (MWNS1 and MWNS2) are obtained and characterised by Fourier transform infrared (FTIR). The effects of reaction temperature, reaction time and maleic anhydride concentration (C_{MAH}) on the carboxylic acid groups value of MWNS have been evaluated. The results show that at a constant temperature the carboxylic acid groups 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 the equilibrium (t_{eq}). When the temperature increased from 25℃ to 77℃, the equilibrium time t_{eq} reduced from 240 min to 150 min and C_{COOH}^{eq} of MWNS increased from 1.94 mmol/g to 2.92 mmol/g. In addition,

C_{COOH}^{eq} of MWNS at 180 min increased from 1.94 mmol/g to 2.80 mmol/g when C_{MAH} increased from 0.5 mol/L to 2.0 mol/L, and it changed a little when C_{MAH} is larger than 2.0 mol/L. We can, therefore, state that the optimum conditions of the MWN modification are as fellow: a reaction temperature of 77℃, a reaction time of 180 min and a concentration of maleic anhydride solution of 2.0 mol/L. Then the concentration of carboxylic acid group will be maximised at 2.80 mmol/g.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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