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# Walnut Shell Modified by Thionyl Chloride and Triethylamine: Synthesis and Characterization

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***Authors' contributions***

*This work was carried out in collaboration among all authors. Author ZM 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 YW managed the literature searches. All authors read and approved the final manuscript.*

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## ABSTRACT

A novel modified walnut shell (TWNS) was prepared through sequentially reacting the walnut shell (WNS) with thionyl chloride and triethylamine in N-methyl pyrrolidone to remove Reactive Brilliant Blue from dye wastewater. Fourier transform infrared (FTIR) and scanning electron microscopy (SEM) were used to characterize the TWNS. The effects of different experimental conditions such as the reaction temperature, the reaction time, the dosage of thionyl chloride and triethylamine on the quaternary ammonium grafting percentage of TWNS have been studied. The results reveal the quaternary ammonium grafting percentage ($Y$) is up to 18.37% when the dosage of thionyl chloride ($V_1$) is 35 mL, the reaction time ($t_1$) is 3 h in the first step reaction; the dosage of triethylamine ($V_2$) is 40 mL, the reaction temperature ($T$) is 80°C and the reaction time ($t_2$) is 12 h in the second step reaction.

*Keywords: Walnut shell; characterization; synthesis.*

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## 1. INTRODUTION

China is a large agricultural country. According to statistics, as many as 700 million tons of agricultural and forestry wastes are generated each year, while less than 350 million tons of agricultural wastes are effectively used, and the utilization rate is very low. Most agricultural and forestry wastes are mainly processed by incineration, causing serious environmental pollution. Therefore, the rational use of agricultural and forestry waste is of great significance to the sustainable development of environmental protection and resource conservation. Various agricultural and forestry wastes such as orange peel [1], pine needle [2], apple pomace [3], almond shell [4], peanut hull [5] and sugarcane bagasse [6] are used due to their low cost, biodegradability, and abundant sources. G.Sai Krishnan et al. [7-11] used cellulose in agricultural and forestry waste to make brake pads and studied its mechanical properties. The production of agricultural and forestry wastes into new materials with specific functions has become more and more popular among researchers.

In China, the annual output of walnuts is about 800,000 tons, which produces a large amount of walnut shell waste. The main components of walnut shells are cellulose, hemicellulose and lignin, of which cellulose accounts for about 31% [12]. Cellulose molecules contain a large number of hydroxyl groups, which can be functionally modified by reacting with hydroxyl groups to meet specific needs. Grafting quaternary ammonium groups on the walnut shell can greatly improve its adsorption capacity for anionic dyes, and the grafting percentage often determines the adsorption capacity of the product [13,14]. Therefore, it is necessary to optimize the process of the walnut shell grafting process to obtain optimal reaction conditions.

In this paper, a novel modified walnut shell (TWNS) was prepared by reaction of thionyl chloride and triethylamine to remove Reactive Brilliant Blue from dye wastewater. The effects of the reaction temperature ($T$), the reaction time ($t_1$, $t_2$), the dosage of thionyl chloride ($V_1$) and triethylamine ($V_2$) on the grafting percentage have been investigated. TWNS was characterized by Fourier transform infrared (FTIR) and scanning electron microscopy (SEM).

## 2. METERIALS AND METHODS

### 2.1 Reagents

Thionyl chloride was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Triethylamine was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. NaOH, HCl, NaCl and N-methyl pyrrolidone were selecting from Shanghai Titian Scientific Co., Ltd. All of them were used straight without further purification and were analytical grade reagents. Walnut shell was collected from a walnut food processing factory. Before reaction, WNS was cleaned using distilled water and dried, and was crushed into particles with a 200-mesh size to the further reaction.

### 2.2 Preparation of TWNS

10 g TWNS powder and 150 mL N-methyl pyrrolidone were added to a 250 mL three-neck flask. Under mechanical stirring, the mixture was heated in a 75°C water bath for 1.5 h. After that, a quantity of pure thionyl chloride ($V_1$) were slowly dripped in the system. The mixture was mechanically stirred, heated and held at 80°C for a time noted ($t_1$), and then sequentially washed with NaOH solution and distilled water around 7, filtered and dried completely at 60°C. And then, the remains were dispersed in a quantity of triethylamine solution ($V_2$) and the mixture was heated at a set reaction temperature ($T$) with mechanical stirring for a time noted ($t_2$). After filtered, the filter cake was washed with water and dried, and the final TWNS product was obtained. Using the controlled variable method, the effects of the reaction time ($t_1$), the dosage of thionyl chloride ($V_1$) in the first step reaction, the reaction temperature ($T$), time ($t_2$), and the amount of triethylamine ($V_2$) in the second step reaction were investigated to determine the optimal reaction conditions.

### 2.3 Determination of Quaternary Ammonium Grafting Percentage

The method for determining the quaternary ammonium grafting percentage ($Y$%) is the weighing method, and the calculation formula is as follows:

$$Y\% = \frac{m_t - m_0}{m_0} \times 100$$

Where $m_0$ (g) represents the weight of modified walnut shell before the second step reaction, $m_t$ (g) is the weight of TWNS after the second step reaction.

## 3. RESULTS AND DISCUSSION

### 3.1 Characterization of TWNS

The FTIR spectra of WNS and TWNS are shown in Fig. 1. The large adsorption peak around 3420 $cm^{-1}$ relates to the stretching of hydrogen bonds in hydroxyl groups. Another adsorption peak at 2950 $cm^{-1}$ is attributed to the stretching of carbon-hydrogen bonds in $-CH_2$ and $-CH_3$. In contrast to WNS, the appearance of sharp adsorption peak at 1458 $cm^{-1}$ in TWNS is the stretching vibration of carbon-nitrogen bonds of $-N^+(C_2H_5)_3Cl^-$ [15,16]. A new adsorption peak around 751 $cm^{-1}$ is attributed to stretching vibration of C-Cl bond [17], due to the unreacted chlorine. The results indicate the quaternary ammonium groups are successfully brought into the surface of WNS.

The SEM images in Fig. 2 demonstrate the surface topography of WNS and TWNS. From the Fig. 2, it’s clear that compared with WNS, the surface of TWNS has wider and longer ravines and more complex porous structures; in other words, the surface area of TWNS increases, indicating TWNS is beneficial to adsorption.

### 3.2 Influencing Factors in the First Step Reaction

#### 3.2.1 Effect of the dosage of thionyl chloride

Due to the existence of a large amount of solvent N methyl pyrrolidone, the low amount of thionyl chloride makes the grafting rate of the reaction product on the low side, and excessive thionyl chloride will cause waste, so 15-40ml is chosen as the research dosage of thionyl chloride. The effect of the dosage of thionyl chloride (15-40 mL) on the grafting rate of quaternary amino groups was investigated when the reaction conditions are as follows: $T$ = 80°C, $t_1$ =3 h, $t_2$ = 8 h, $V_2$ = 50 mL. The result was shown in Fig. 3. As shown in Fig. 3, as the dose of thionyl chloride increased, the grafting rate of quaternary amino groups showed a tendency to increase first and then began to balance at 35 mL. This shows that when the amount of thionyl chloride exceeds 35 mL, the reactants are excessive and the reaction conversion rate remains basically unchanged. Therefore, the dose of thionyl chloride in the first reaction was controlled to 35 mL.

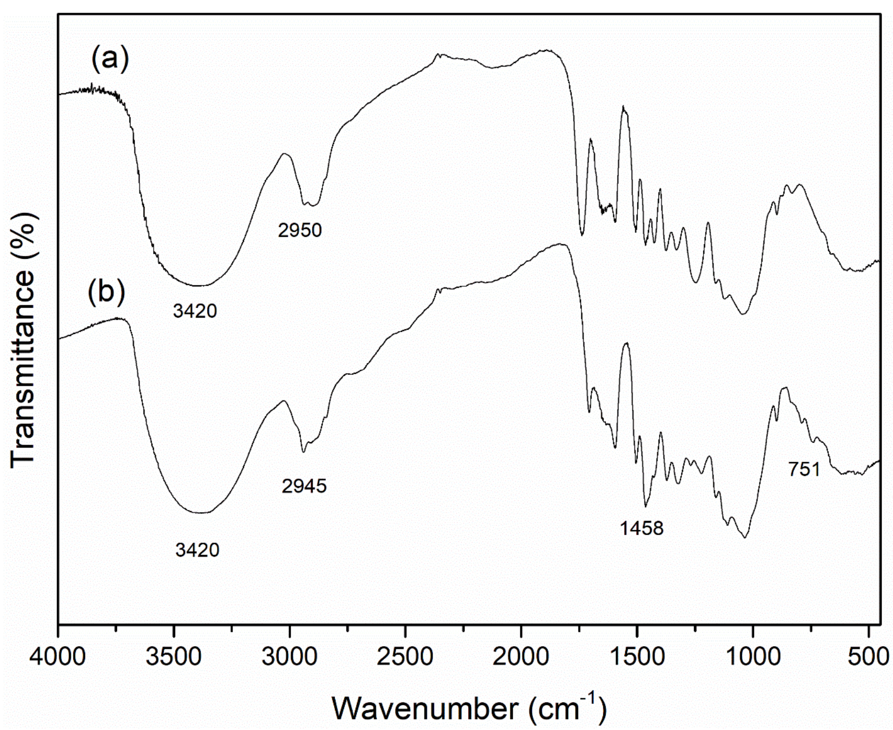


**Fig. 1. FTIR spectra of WNS (a) and TWNS (b)**

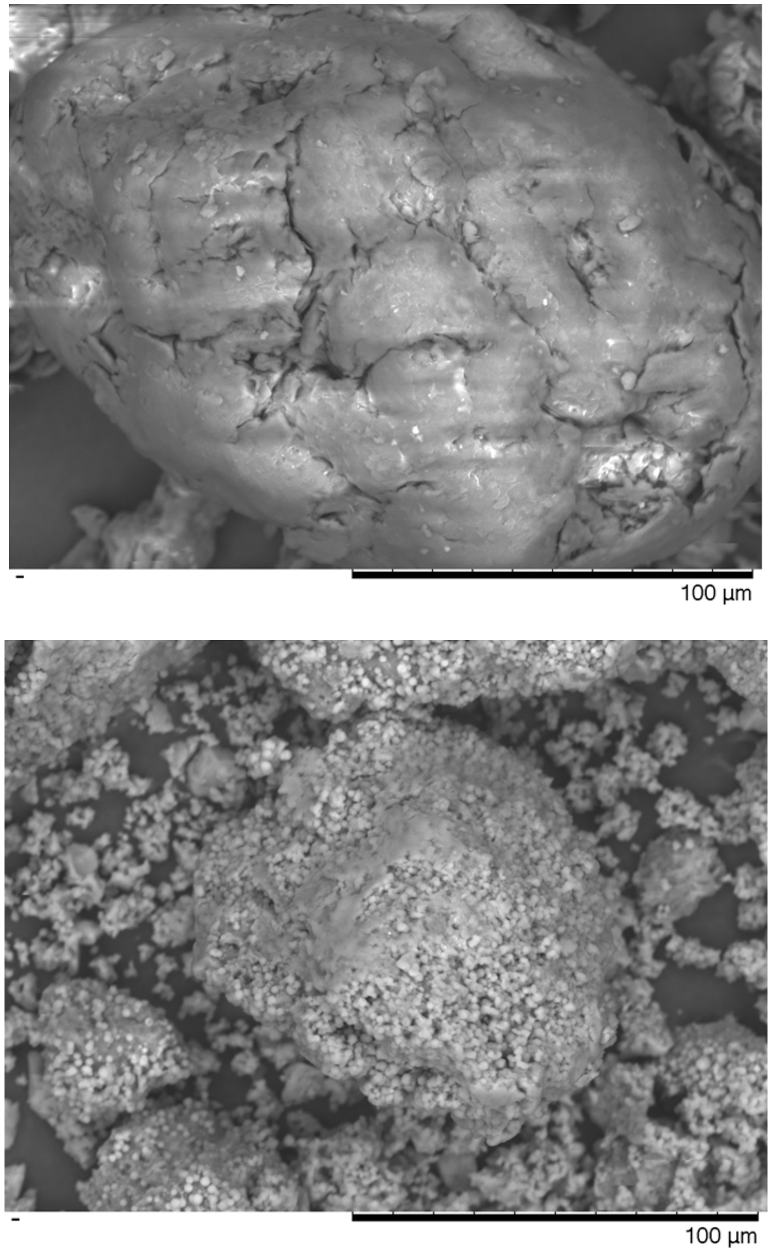


**Fig. 2. SEM images of (a) WNS and (b) TWNS**

#### 3.2.2 Effect of reaction time

The effect of reaction time (60-300 min) on the grafting rate of quaternary amino groups was investigated when the reaction conditions are as follows: $T$ = 80°C, $t_2$ = 8 h, $V_1$ = 35 mL, $V_2$ = 50 mL. The result was shown in Fig. 4. As shown in Fig 4, with the reaction time increasing, the grafting rate of quaternary amino groups increased first and then gradually balanced at 3 h. This shows that the reaction reached equilibrium after 3 hours. Therefore, the reaction time in the first reaction was controlled to 3 h.

### 3.3 Influencing Factors in the Second Step Reaction

#### 3.3.1 Effect of reaction temperature

The effect of reaction temperature (60-90°C) on the grafting rate of quaternary amino groups was studied when the reaction conditions are as follows: $t_1$ = 3 h, $t_2$ = 8 h, $V_1$ = 35 mL, $V_2$ = 50 mL.

The result was shown in Fig. 5. As shown in Fig. 5, with the reaction temperature increasing, the grafting rate of quaternary amino groups presented a trend of first increasing and then decreasing, and reached the highest value at 80°C. This may be because before 80°C, the reaction rate increases with the increase of temperature, the reaction is not balanced, the reaction conversion rate increases with the increase of temperature, and the grafting rate increases; After 80°C, the reaction is exothermic, the temperature increases, the conversion rate decreases, and the grafting rate also decreases. Therefore, the reaction temperature in the second reaction was controlled to 80°C.

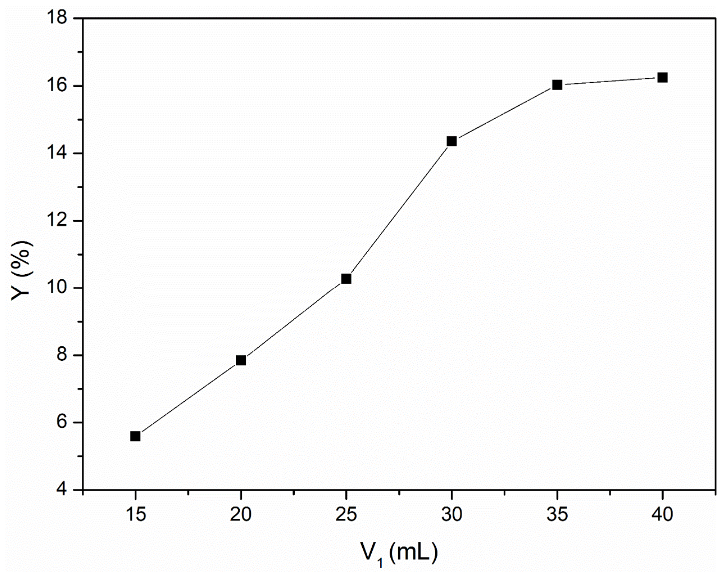


**Fig. 3. Effect of the dosage of thionyl chloride in the first step reaction on the grafting rate of quaternary amino groups**

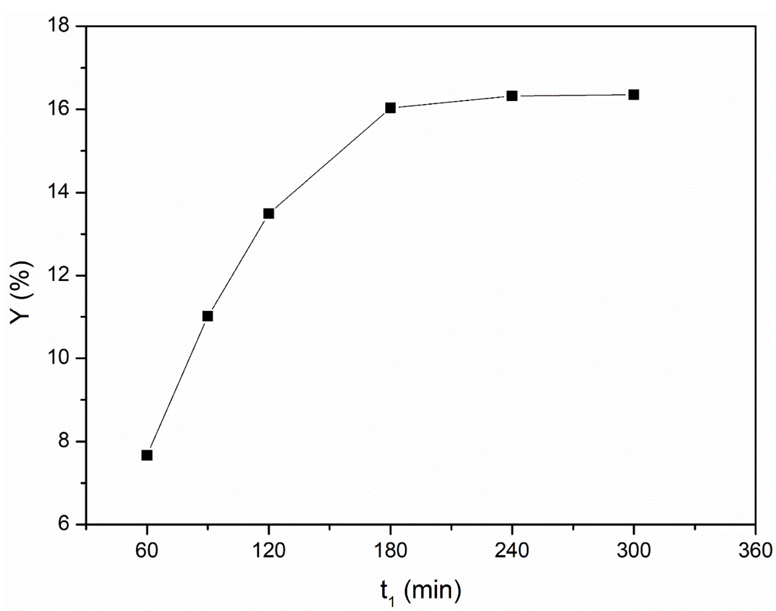


**Fig. 4. Effect of reaction time in the first step reaction on the grafting rate of quaternary amino groups**

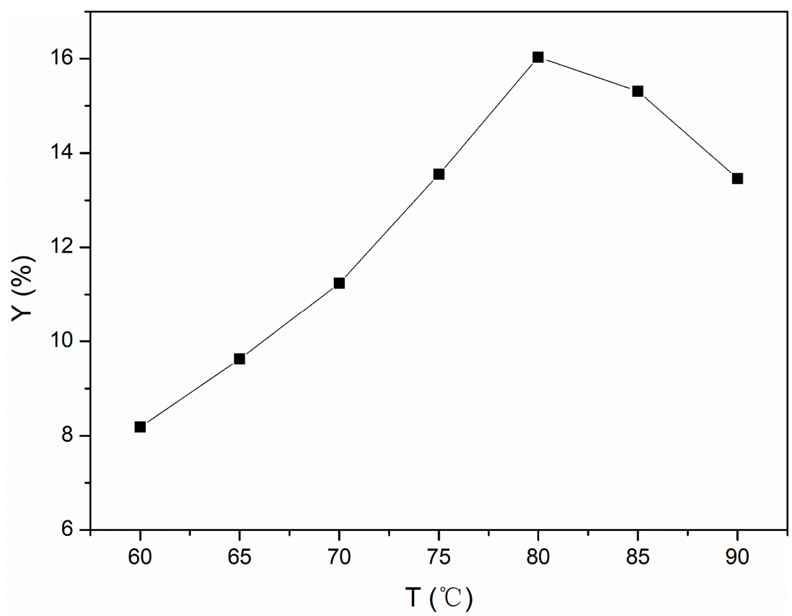


**Fig. 5. Effect of reaction temperature in the second step reaction on the grafting rate of quaternary amino groups**

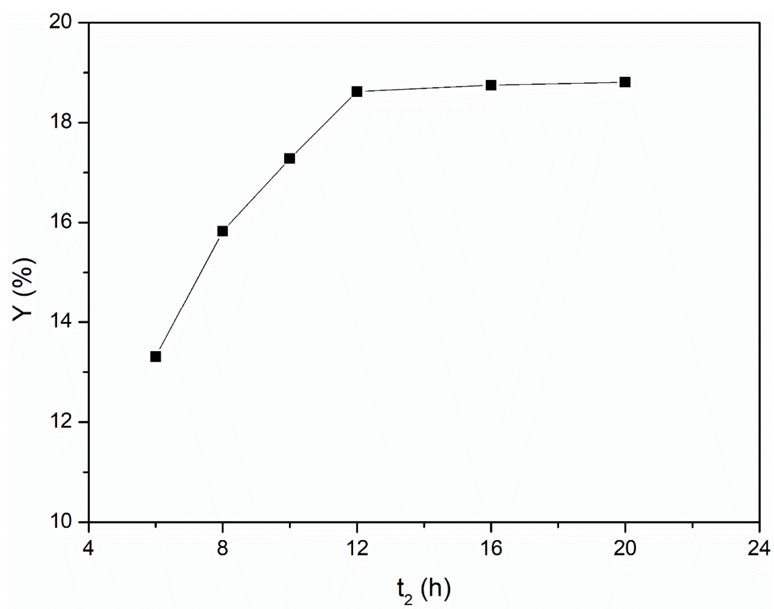


**Fig. 6. Effect of reaction time in the second step reaction on the grafting rate of quaternary amino groups**

#### 3.3.2 Effect of reaction time

The effect of reaction time (6-20 h) on the grafting rate of quaternary amino groups was studied when the reaction conditions are as follows: $T$ = 80°C, $t_1$ = 3 h, $V_1$ = 35 mL, $V_2$ = 50 mL. The result was shown in Fig. 6. As shown in Fig. 6, with the extension of time, the grafting rate of quaternary amino groups first increased and then gradually balanced, and increased slowly after 12h. This shows that the reaction reached equilibrium after 12 hours, so the subsequent second step reaction time was set to 12 h.

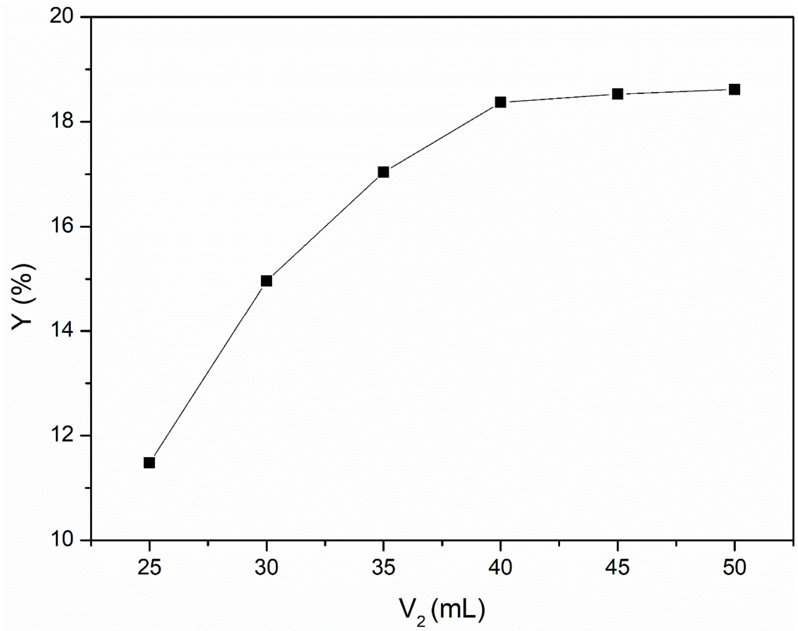


**Fig. 7. Effect of the dosage of triethylamine in the second step reaction on the grafting rate of quaternary amino groups**

### 3.3.3 Effect of the dosage of triethylamine

The effect of the dosage of triethylamine (25-50 mL) on the grafting rate of quaternary amino groups was investigated when the reaction conditions are as follows: $T$ = 80°C, $t_1$ =3 h, $t_2$ = 12 h, $V_1$ = 35 mL. The result was shown in Fig. 7. As shown in Fig. 7, as the dose of triethylamine increased, the grafting rate showed a trend of increasing first from 25 to 40 mL and changing slowly from 40 to 50 mL. This shows that when the amount of triethylamine exceeds 40 mL, the reactants are excessive and the reaction conversion rate remains basically unchanged. Therefore, the dose of triethylamine in the second reaction was controlled to 40 mL.

## 4. CONCLUSION

A new type of adsorbent (TWNS) was synthesized by chemical modification of walnut shell with thionyl chloride and triethylamine for the removal of RB-19 from aqueous medium. The TWNS was characterized through FTIR spectroscopy and SEM. The effects of reaction temperature ($T$), the reaction time ($t_1$, $t_2$), the dosage of thionyl chloride ($V_1$) and triethylamine ($V_2$) on the quaternary ammonium grafting percentage of TWNS have been evaluated. The results shown that the optimal reaction conditions were as follows: in the first step reaction, the dosage of thionyl chloride ($V_1$) is 35 mL, the reaction time ($t_1$) is 3 h; in the second step reaction the dosage of triethylamine ($V_2$) is 40 mL, the reaction temperature ($T$) is 80°C and the reaction time ($t_2$) is 12h.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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