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Preparation of cellulose sponge from waste newspaper

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Abstract. Using cellulose extracted from waste newspaper as raw material, NaOH/urea aqueous solution as solvent, anhydrous sodium sulfate as pore-forming agent, cellulose sponge with super absorbent capacity was prepared by freezing method, and hydrophobic cellulose sponge was prepared by immersing cellulose sponge into hydrolysate of cetyltrimethoxysilane with different composition. The water absorption and oil absorption of water-absorbent and hydrophobic cellulose sponge samples were tested and characterized by infrared and X-ray diffraction. The results showed that the water absorption of water-absorbent cellulose sponge could reach 560 wt% under the conditions of 3 g of microcrystalline cellulose, 15 g of pore-forming agent and 50 g of NaOH/urea solution. Hydrophobic cellulose sponge was prepared by hydrolysis of hexadecyl trimethoxysilane/SiO₂, and the best oil rate was 157 wt%.

1. Introduction

China's paper production and consumption have reached the first in the world. The reuse of waste paper has become the main way of paper making in China. At present, recycled pulp accounts for 64% of the total pulp consumption in China. With the increase of paper use and waste paper quantity, research on waste newspapers is one of hot issue in academy^[1]. Newspapers contain a large amount of cellulose, which is a renewable resource in nature. As a natural macromolecule material, cellulose is synthesized about 150 billion tons per year. In recent years, with the decline of the reserves of non-renewable resources such as oil and coal and the destruction of the environment by the production process^[2], more attention has been paid to the environmental protection and pollution-free cellulose resources.

Wu et al use microcrystalline cellulose as material, combed cotton as reinforcing fiber, NaOH/urea aqueous solution as solvent, and anhydrous sodium sulfate as pore-forming agent to produce cellulose sponge. This sponge has high water absorption and is widely used in industry, agriculture, cleaning, medical treatment and automotive shock absorbent fields^[3]. In this paper, water-absorbent cellulose sponge and hydrophobic cellulose sponge were prepared from waste newspaper in order to further expand the utilization and value of waste newspaper.

2. Experimental

2.1. Materials

Anhydrous ethanol, isopropyl titanate, ethyl orthosilicate, concentrated ammonia water, glacial acetic acid, nitric acid, hydrochloric acid with analytical purity were purchased from Chemical Reagent Co.,



Ltd. of China Pharmaceutical Group. Toluene and hexadecyl trimethoxysilane (HTDMS) were got from Wuxi Longjili Chemical Reagent Co., Ltd and Aladdin Reagent Co., Ltd, respectively. Rapeseed oil was used directly without further purification.

2.2. Preparation of hydrophilic cellulose sponge

2.2.1. Preparation of microcrystalline cellulose. Microcrystalline cellulose prepared from waste newspaper was got by the following steps: pretreatment of waste newspaper, extraction of alpha-cellulose and preparation of microcrystalline cellulose. Experimental methods were specified in the reference^[4].

2.2.2. Preparation of cellulose sponge. Different weight of microcrystalline cellulose was added in 50 g of NaOH/urea solution with stirring. The mixture was placed under the condition of ice-water solution at 261.15K, sodium sulfate was further added with stirring, and then put into the freezer for aging. The frozen cellulose sponge was washed at 353.15K.

$$\text{Water absorption rate} = (W_1 - W_2) / W_2 \times 100\%$$

where W_1 is the wet weight of water absorbent cellulose sponge in the unit of g, W_2 is dry weight of cellulose sponge sample in the unit of g.

2.3. Preparation of hydrophobic cellulose sponge

2.3.1. Preparation of HTDMS Hydrolysate. HTDMS hydrolysate was prepared by mixing 15 ml of toluene solution in 50 ml beaker, adding 0.65 ml of HTDMS, 2 ml of distilled water, stirring at room temperature on magnetic stirrer, adding 0.5 ml of glacial acetic acid, stirring again, and reacting in water bath at 333.15K.

2.3.2. Preparation of SiO_2 Sol. 50 ml of ethanol and 2-4 ml of ammonia water were added to the three-neck flask under stirring. The flask was heated in a water bath at 333.15K. Ethyl orthosilicate was added into the mixed solution after homogeneous stirring. Milky white SiO_2 sol was obtained after aging for 24 hours.

2.3.3. Preparation of TiO_2 Sol. 10 ml of isopropyl titanate was slowly added to the flask after mixing 80 ml of ethanol and 0.4 ml of nitric acid. 3 ml of distilled water, 0.2 ml of glacial acetic acid and 10 ml of ethanol were added to the flask drop by drop, and the TiO_2 sol was obtained by stirring in a water bath at 313.15K for 2 h.

2.3.4. Preparation of Hydrophobic Cellulose Sponge. Cellulose sponges were immersed in the hydrolysate of HTDMS, and then reacted in water bath at 333.15K. After the reaction, was completed, the sponges were removed and dried at 353.15K after the reaction. Hydrophobic cellulose sponges modified by silane were prepared. Silanized SiO_2 hydrophobic cellulose sponge and silanized TiO_2 hydrophobic cellulose sponge were prepared by adding 4 ml of SiO_2 sol or TiO_2 sol, respectively^[5].

$$\text{Oil absorption rate} = (W_3 - W_4) / W_4 \times 100\%$$

where W_3 is the wet weight of hydrophobic cellulose sponge in the unit of g, W_4 is dry weight of hydrophobic cellulose sponge sample in the unit of g.

3. Results and Discussion

3.1. Effect of Microcrystalline Cellulose Dosage on Water Absorption Rate

The effect of microcrystalline cellulose dosage on the water absorption rate of cellulose sponge is shown in Fig. 1. It can be seen from Fig. 1 that the water absorption rate of cellulose sponge made from market cellulose raised to about 640 wt% at the first stage under the conditions of 15 g of pore-forming agent and 50 g of NaOH/urea solution, with the addition of microcrystalline cellulose from 2

g to 5 g. The rate then decreased to 570 wt%. Similarly, the water absorption rate of cellulose sponge made from waste newspaper cellulose also rose to about 560 wt% at first, then reduced to 460 wt% gradually. When the dosage of porous agent is constant, the amount of cellulose sponge produced at low microcrystalline cellulose content is very small, which led to a low water absorption rate. With the increase of cellulose concentration, the density of cellulose sponge increases, the porosity decreases, and the water absorption decreases^[6]. With the increase of the amount of microcrystalline cellulose, the water absorption decreases gradually.

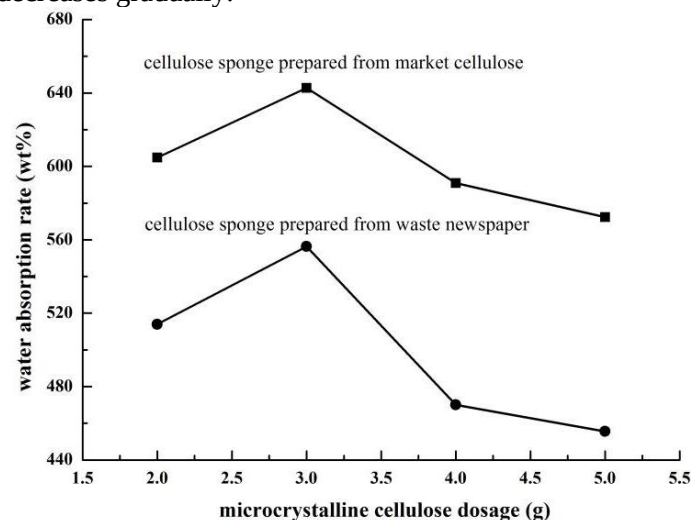


Figure 1. Effect of microcrystalline cellulose dosage on the water absorption rate.

3.2. Effect of Pore-forming Agent Dosage on Water Absorption Rate

The effect of pore-forming agent dosage on the water absorption of cellulose sponge is shown in Fig. 2. As Fig. 2 shows that the water absorption rate of cellulose sponge prepared from market cellulose or waste newspaper cellulose indicate an upward trend with the increase of the amount of pore-forming agent from 12 g to 15 g under the conditions of 3 g of microcrystalline cellulose and 50 g of NaOH/urea solution. The water absorption range of cellulose sponge prepared from market cellulose give an upward trend from 620 wt% to 640 wt%, when that of cellulose sponge made from waste newspaper increased from 530 wt% to 560 wt%. This is due to the density of cellulose sponge decreases with the increase of the amount of pore-forming agent, and the porosity of cellulose sponge increases accordingly^[6].

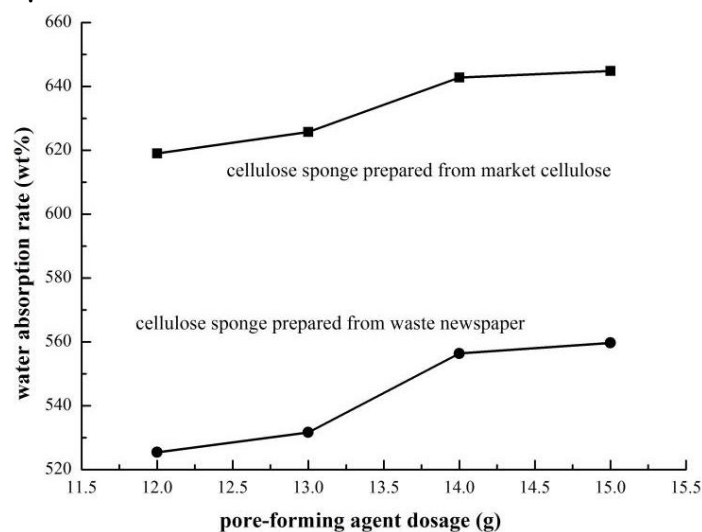


Figure 2. Effect of pore-forming agent dosage on the water absorption rate.

3.3. FT-IR Characterization

Fig. 3 is the FT-IR spectrum of cellulose sponge from market cellulose. It could be seen that HTDMS cellulose sponge has a characteristic peak of C-O bond at 1062 cm^{-1} , where the absorption peak of Si-O-Si bond is covered by the characteristic peak of C-O bond. HTDMS has silylated the cellulose sponge successfully, as the spectra of sample c, sample a and sample b show obvious changes. The absorption peak of sample b is 1062 cm^{-1} , the bending and rolling peaks of Si-O-Si bond at 800 cm^{-1} and 460 cm^{-1} are strengthened respectively. In addition to the obvious characteristic absorption peak of Si-O-Si at 1057 cm^{-1} , a weak absorption peak of Ti-O-Si bond can be observed at 907 cm^{-1} . It is proved that titanium dioxide enters Si-O-Si structure and participates in bonding^[7].

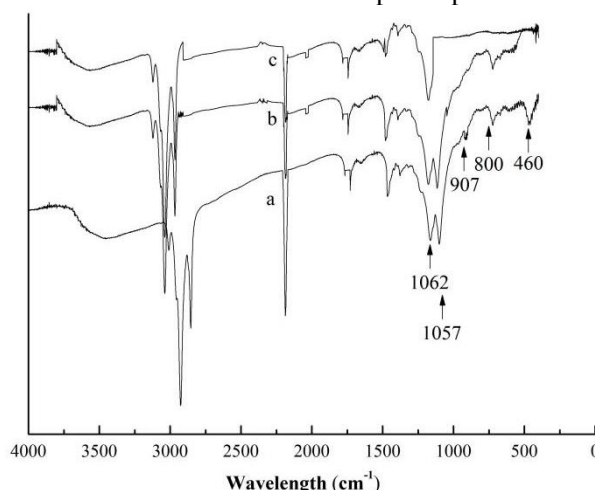


Figure 3. FT-IR spectrum of cellulose sponge prepared from market cellulose: (a) HTDMS/TiO₂ cellulose sponge; (b) HTDMS/SiO₂ cellulose sponge; HTDMS cellulose sponge.

Fig. 4 is FT-IR spectrum of cellulose sponge from waste newspaper. As shown in Fig. 4, the characteristic peaks of HTDMS/titanium dioxide cellulose sponge prepared from waste newspaper are more obvious than that from market cellulose. There is an obvious C-O characteristic peak at 1062 cm^{-1} and a weak absorption peak at 907 cm^{-1} , which is the characteristic peak of Ti-O-Si bond. It is proved that titanium dioxide enters Si-O-Si structure and participates in bonding^[7]. Absorption peaks at 1062 cm^{-1} of b increased significantly, and the bending and rolling peaks at 800 cm^{-1} and 460 cm^{-1} were Si-O-Si bonds, respectively.

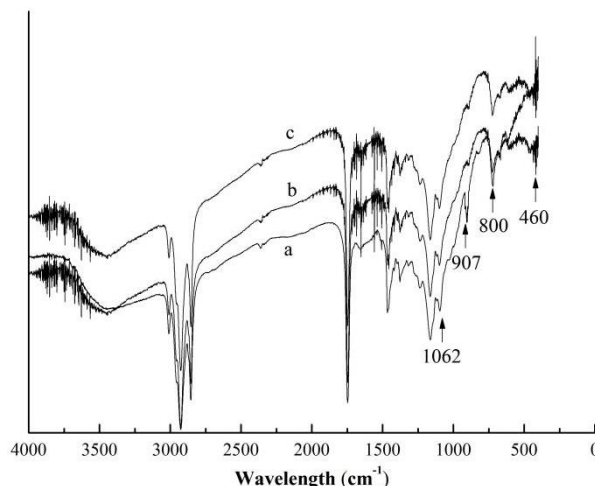


Figure 4. FT-IR spectrum of cellulose sponge prepared from waste newspaper: (a) HTDMS/TiO₂ cellulose sponge; (b) HTDMS/SiO₂ cellulose sponge; HTDMS cellulose sponge.

3.4. XRD Characterization

Fig. 5 is the XRD spectrum of different cellulose samples. It could be shown that the superhydrophobic sponge prepared from waste newspaper is similar with that of microcrystalline cellulose and the cellulose microcrystalline cellulose with the best process. Diffraction peaks at 2θ of 21° , 23.5° and 34.5° had a good uniformity. The diffraction area of microcrystalline cellulose is larger than that of α -cellulose, which shows that the crystallinity of microcrystalline cellulose is higher than that of α -cellulose. The crystallinity of super absorbent cellulose sponge is lower. Compared with other processes, microcrystalline cellulose got from worst process has difference. This indicates that the sample has been over hydrolyzed, which destroyed the cellulose structure and reduced the crystallinity^[8].

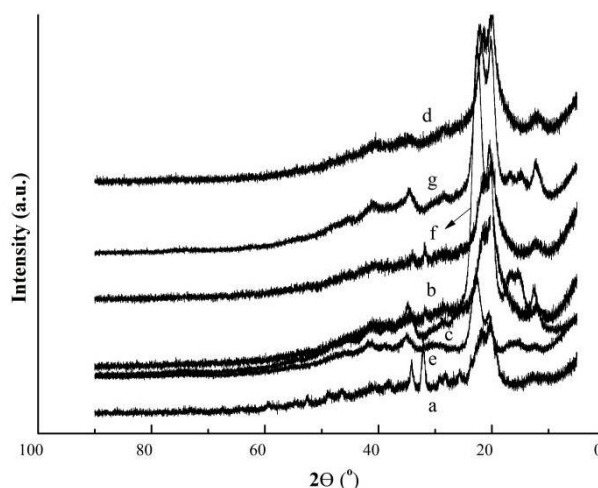


Figure 5. XRD patterns: (a) super absorbent waste newspaper cellulose sponge; (b) microcrystalline cellulose with the worst yield; (c) microcrystalline cellulose with the best process; (d) HTDMS/SiO₂ waste newspaper cellulose sponge; (e) HTDMS/waste newspaper cellulose sponge; (f) α -cellulose; (g) HTDMS/TiO₂ waste newspaper cellulose sponge.

3.5. Oil Absorption Rate of Hydrophobic Cellulose Sponge

The oil absorption rate of hydrophobic cellulose sponge prepared by different methods was tested. The experiment was repeated three times in each group. The average value was obtained and the variance was calculated. The oil absorption rate of hydrophobic cellulose sponge was shown in Fig. 6.

It is shown from the Fig. 6 that hydrophobic cellulose sponges modified by HDTMS, HDTMS/SiO₂, HDTMS/TiO₂ have excellent oil absorption properties. The difference between oil absorption of hydrophobic cellulose sponges made from market cellulose and that made from waste newspaper cellulose is less than 10 wt%. SiO₂ has a certain oil absorption capacity^[9]. The oil absorption rate of microcrystalline cellulose sponge modified with HDTMS/SiO₂ is the best. The oil absorption rate of hydrophobic cellulose sponge made from market cellulose is about 194 wt%. The oil absorption rate of hydrophobic cellulose sponge made from waste newspaper cellulose is as high as 157 wt%. The quality of oil absorbed is up to 1.5 times than that of dry weight.

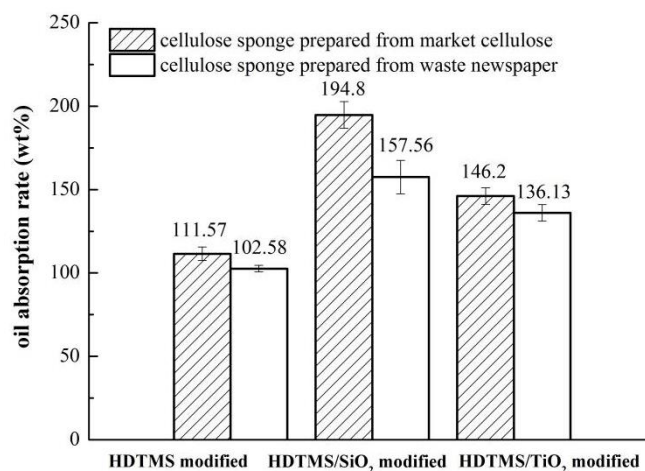


Figure 6. Oil absorption rate of hydrophobic cellulose sponge.

4. Conclusions

Cellulose sponge with super absorbency was prepared by using cellulose extracted from waste newspaper, NaOH/urea aqueous solution as solvent and anhydrous sodium sulfate as pore-forming agent. Cellulose sponge with high hydrophobicity could be got by immersing in hydrolysate of hexadecyltrimethoxysilane with different composition after modifying.

The absorbent cellulose sponge prepared from waste newspaper cellulose can absorb water up to 560 wt% in the conditions of 50 g NaOH/urea solution, 3 g microcrystalline cellulose and 15 g pore-forming agent. The hydrophobic cellulose sponge prepared by modified HDTMS/SiO₂ has the best oil absorption rate up to 157 wt%.

The microcrystalline cellulose extracted from waste newspaper has the same properties as the microcrystalline cellulose sold in the market in the preparation of cellulose sponge, which lays a good foundation for the maximum utilization of cellulose resources in waste newspaper.

Acknowledgments

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