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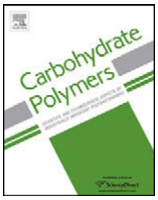

Short communication

Preparation and characterization of Konjac glucomannan-based cation exchange resin

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ABSTRACT

The granular Konjac glucomannan-based cation exchange resin with different pore diameters was synthesized by a low-cost way. The pore diameters could be controlled subtly by regulating the ratio of benign solvent (water) and expansion inhibitor (ethanol). The resin was characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Its physical parameters were evaluated as well. The results indicated that the cross-linking reaction of Konjac glucomannan phosphate (KGMP) made the surface uneven and brought out a little fold-like structure that was beneficial to the water retention capacity and resin exchange capacity.

1. Introduction

Synthesis, characterization, and ion exchange studies of polymeric resins deserve to be investigated because of their varied characteristics and beneficial properties (Masram, Bhave, & Kariya, 2010). Now ion exchangers have been widely used in hydrometallurgy, separation of radioisotopes, synthetic chemistry, biomedical engineering and antibiotic purification and so on. For instance, the proteins of low molecular weight such as phosvitin, cytochrome *c* and ribonuclease A have been separated (Castellani, Martinet, David-Briand, Guerin-Dubiard, & Anton, 2003; Tweeten & Tweeten, 1986).

Although ion exchange resins were applied extensively, the research indicated that synthetic of ion exchange resins were unsuitable for the separation of biomacromolecule such as protein, nucleic acid, and polysaccharide. In order to overcome above disadvantages, a hydrophilic resin with lower charge density and large pore diameter should be exploited. In 1950, two sorts of hydrophilic and macroporous ion exchangers, carboxymethylcellulose and diethyl aminoethyl cellulose, were synthesized by Peterson and Sober (1956). Subsequently, glucan-based and agarose-based ion exchange resins were exploited. However, some drawbacks for these types of ion exchange resins, such as complicated granulating process and single functional groups, tremendously restrict their application in industry.

Intensive studies have been performed to find low-cost and effective materials for ion exchange resin. Of all these materials, Konjac glucomannan (KGM) has been considered as one of the most abundant and available raw materials. KGM is a low-cost high-molecular-weight water-soluble nonionic heteropolysaccharide obtained from the tubers of Amorphophallus Konjac plants (Li & Xie, 2004; Li et al., 2009). Its main chain consists of β-1,4 linked D-mannose and D-glucose units with a low degree of acetyl groups (Liu, Hu, & Zhuo, 2004; Liu et al., 2010), and it has been generally used in food, medical or chemical engineering, and other fields because of its unique physical and chemical properties (Li et al., 2009). KGM has the granular structure of its own, good hydrophilicity, large specific surface area, is a great source of industrial application prospect of the carrier.

In this article, the granular cation exchange resins with different pore diameters are synthesized by controlling the ratio of benign solvent (water) and expansion inhibitor (ethanol) ingeniously. This method avoids the complex process, such as complicated granulating process, that greatly reduces the costs. This study not only provides a novel way to prepare low-cost ion exchange resin, but a new idea for scientific application of KGM.

2. Materials and methods

2.1. Materials

KGMP (degree of substitution = 0.17) was prepared as our previous work (Wang, Ye, Li, & Xie, 2009). Sodium trimetaphosphate was purchased from Aladdin Reagent Company. Sodium chloride

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and absolute ethyl alcohol were purchased from Sinopharm Chemical Reagent Company. They were all of A.R. grade and used without further purification.

2.2. Preparation of Konjac glucomannan-based cation exchange resin

KGMP (75 g), 500 mL ethanol solution with different concentrations [45%, 50%, 55%, 60%, and 70% (v/v)], sodium trimetaphosphate (2.8 g) as a cross-linking agent, and sodium chloride (4.2 g) in a three-neck reaction flask were stirred magnetically at 75 °C for 1 h at the hermetic state. Then 4 g sodium hydroxide was added with stirring. After 2 h, the solution was taken to pH 7.0 by gentle addition of hydrochloric acid. To the reaction product, 30% ethanol aqueous solution was added to remove the residual reagent. The resulting product was additionally washed with aqueous ethanol [50%, 70%, 80%, and 95% (v/v)] successively and then dried at 60 °C to constant weight. Then a series of cation exchange resins were obtained and coded as CL-45, CL-50, CL-55, CL-60, and CL-70. Moreover, they were collectively referred to as CL-KGMPs.

2.3. Physical parameters measurement

2.3.1. Resin pretreatment

Resin was immersed in distilled water and intermittently mixed with a magnetic stirrer for 2 h, and then the supernatant was discarded. After the procedure was repeated five times, the resin was treated with hydrochloric acid and sodium hydroxide, respectively, and each step followed by washing with distilled water until neutral. Finally, the resin was treated with hydrochloric acid again and washed with water until neutral.

2.3.2. Water retention capacity measurement (GB 5757-86)

Dehydration samples (m_1/g) was dried at 105 °C for 2 h and weighed (m_2/g). The water retention capacity (X/%) of resin was calculated from $X = (m_1 - m_2)/m_2$.

2.3.3. Bulk and true density of resins in wet state measurement (GB 8331-87, GB 8330-87)

Distilled water was added into ion exchange density meter, the weight of them was marked as m_1. Subsequently, some dehydration resin was added and the total weight was marked as m_2. Then the volume of resin (V'/mL) was recorded, and V' needed correction into apparent volume (V_b), the bulk density of resins in wet state (d_B) was calculated from $d_B = (m_2 - m_1)/V_b$. The weight of ion exchange density meter which continue to fill up with distilled water was marked as m_4. The weight of density meter full with distilled water was marked as m_3. The true density of resins in wet state (d_T) was calculated as:

$$d_T = \frac{(m_2 - m_1) \times d_w}{(m_2 - m_1) - (m_4 - m_3)}$$

where d_w is the density of water at test temperature.

2.3.4. Resin exchange capacity measurement (GB 8144-87)

Dehydration resin (M/g) and 0.1 M sodium hydroxide (100 mL) were mixed in conical flask with stopper and placed in water bath at 60 °C for 2 h. After environmental cooling to room temperature, 25 mL supernatant, 50 mL distilled water, and three drops methyl red-time methylene blue mixed indicator were added into conical flask. The product was titrated with hydrochloric acid standard solution and the endpoint of titration was indicated by solution maintaining red for 15 s without fading. The exchange capacity of wet resin (Q'_T) was calculated as:

$$Q'_T = \frac{4(V_2 - V_1)C_{HCl}}{M}$$

where V_1 and V_2 are the supernatant and blank test consumption volume of hydrochloric acid standard solution, respectively; C_{HCl} is the concentration of hydrochloric acid standard solution.

And the exchange capacity of dry resin (Q_T) was calculated from $Q_T = Q'_T/(1 - X)$.

2.3.5. Swelling degree measurement

Six colorimetric cylinders (10 mL) were numbered from one to six and cation exchange resins (W/g) were added. Subsequently, sodium chloride solution (10 mL) with different concentrations (0, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0 mol/L) were added, respectively and shaken up. Then the volume of resin (V/mL) was recorded after 24 h. The swelling degree (S) of resin was calculated from $S = V/W$.

2.4. Characterization

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

The powdered CL-KGMPs were blended with potassium bromide and laminated, and the IR of the resin was recorded at room temperature using a Nicolet (USA) Nexus 470 FTIR spectrometer at a resolution of 4 cm^{-1} in the range of 400–4000 cm^{-1} (Duarte, Ferreira, Marvao, & Rocha, 2002; Focher, 1990).

2.4.2. Scanning electron microscopy (SEM)

The microstructure of a dry CL-KGMPs sample was investigated by means of a scanning electron microscope (SEM, JSM-6390/LV). The dry sample was ground into powder, mounted on a metal stub, and coated with gold. Subsequently, its microstructure was observed by SEM.

3. Results and discussion

3.1. Physical parameters

The study of physical parameters was primary importance for determining the performance of resins. The physical parameters dependence of ethanol concentration was such that the best water retention capacity (X/%) was observed when the ethanol concentration was 45% (Table 1). In general, water retention capacity was influenced by the microstructure of CL-KGMPs (Section 3.4). In presence of 60% ethanol, the true and bulk density of resins in wet state (d_B and d_T) both achieved peak value. The low degree of substitution of KGMP might be caused the resin exchange capacity of wet resin (Q'_T) was only 0.338 mmol/g; moreover, the water retention capacity also affected Q'_T. Table 1 presented higher water retention capacity gives rise to lower Q'_T. The CL-45 showed the

Table 1
The physical parameters of CL-KGMPs.

	CM sephadex C-25	CL-45	CL-50	CL-55	CL-60	CL-70
X (%)	–	98.56 ± 0.150	93.45 ± 0.180	89.06 ± 0.120	87.23 ± 0.400	88.44 ± 0.180
d_B (g/mL)	–	1.003 ± 0.001	1.041 ± 0.000	1.043 ± 0.002	1.051 ± 0.008	1.040 ± 0.000
d_T (g/mL)	–	0.587 ± 0.000	0.588 ± 0.013	0.610 ± 0.002	0.635 ± 0.005	0.617 ± 0.009
Q'_T (mmol/g)	0.55	0.077 ± 0.004	0.138 ± 0.003	0.203 ± 0.005	0.338 ± 0.032	0.216 ± 0.018
Q_T (mmol/g)	4.5 ± 0.5	5.686 ± 0.290	2.081 ± 0.017	1.846 ± 0.019	2.648 ± 0.242	1.867 ± 0.163

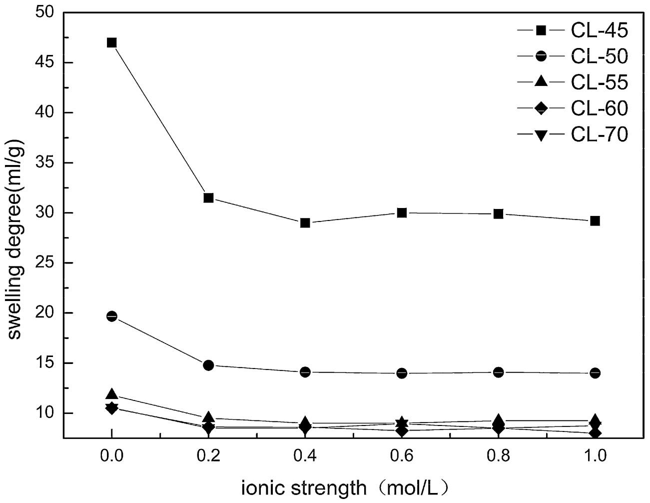

Fig. 1. Effect of ionic strength on swelling degree of CL-KGMPs.

optimal exchange capacity of dry resin (Q_T) which is superior to CM sephadex C-25 (4.5 mmol/g), which can be explained as its large aperture made the exchanger exposed adequately under ion exchange.

3.2. Swelling degree of CL-KGMPs

Fig. 1 shows the swelling degree dependence of the ionic strength. It can be seen that the swelling degree of CL-45 was significantly higher than others and the trends of all samples were similar. This result agrees with the expected behavior. It is well known that the swelling degree has a relation to ionic strength. The negative

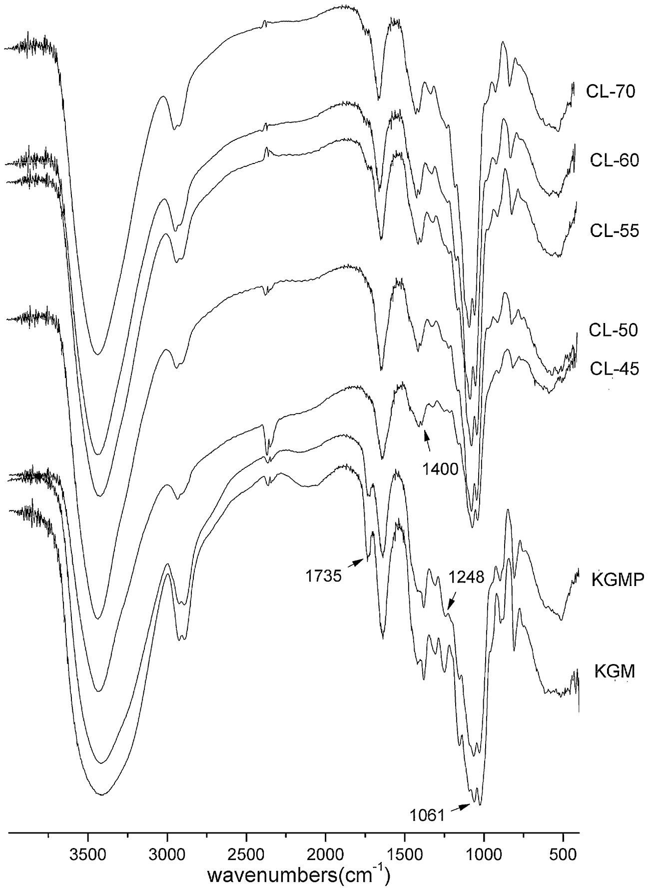

Fig. 2. FTIR spectra of KGM, KGMP, and CL-KGMPs.

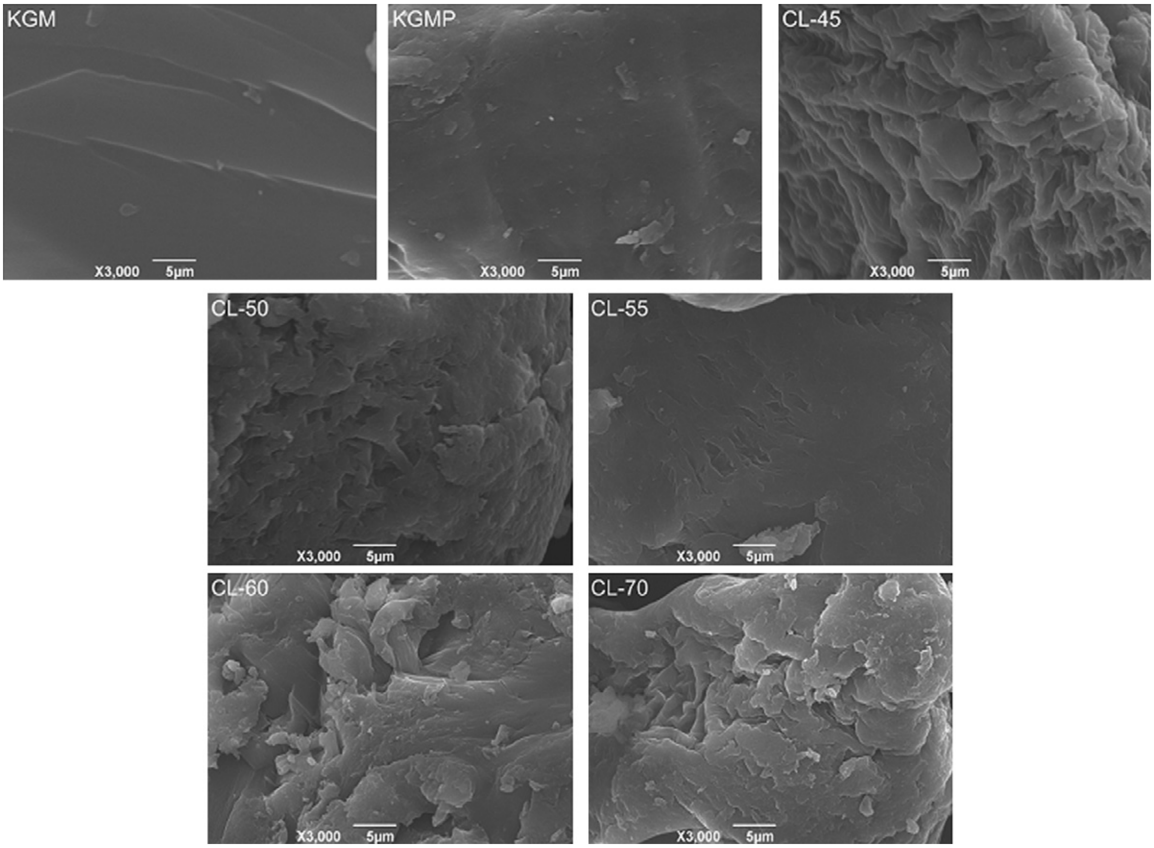

Fig. 3. SEM images of KGM, KGMP, and CL-KGMPs.

charged functions brought by the sodium trimetaphosphate gives rise to an increase of swelling degree. However, increasing ionic strength minimizes the repulsion effect by screening the negative charges and swelling degree is thus reduced (Liu, Fan, Wang, & He, 2008). Further more, at low concentration of ethanol, KGMP has relatively high swelling characteristics that contributes to cross-linking reaction, and then can form a certain network structure that can enhance the water retention capacity as well as the swelling degree. Besides, the formation of relatively compact structure, has certain unfavorable effects on the water retention capacity and swelling degree, as a result of the low swelling characteristics brought by the high concentration of ethanol.

3.3. FT-IR

The IR spectra of the resins of KGM, KGMP, CL-45, CL-50, CL-55, CL-60, and CL-70 were shown in Fig. 2. It can be seen that the absorption band of P=O stretching at 1400 cm^{-1} and the band at 1061 cm^{-1} was assigned to the stretching of C–O. For the IR spectra of KGMP, comparing with spectrum of KGM, some peaks appeared, became stronger or weaker due to interaction or superposition of peaks among groups of KGM and KGMP. The presence of the band at 1400 cm^{-1} and the enhancement of the band at 1061 cm^{-1} confirm that the formation of KGMP. Comparing the CL-KGMPs spectrum with that of KGMP, because the decrease of phosphate esterification of hydroxyl results in the absorption band at 1248 cm^{-1} become weaker. And the absorption band of carbonyl of acetyl groups disappeared, the reason might be deprivation of the acetyl groups in the alkaline environment. However the band of P=O stretching become stronger due to the superposition of peaks of phosphate bond.

3.4. SEM

The SEM photographs of KGM, KGMP, and CL-KGMPs are presented in Fig. 3. SEM photographs indicate that unmodified KGM has smoothing surface, but it shows coarseness due to the phosphate esterification of KGM, and the results are consistent with previous research (Chen, Liu, Chen, & Zhuo, 2005). The surface became uneven and brought out a little fold-like structure when KGMP was crosslinked with sodium trimetaphosphate, thereby specific surface area increased significantly. And SEM images showed that CL-KGMPs' water retention capacity had a certain relation to the specific surface. Great specific surface, caused by porous structure, was beneficial to water retention capacity.

4. Conclusions

The granular Konjac glucomannan-based cation exchange resin with different pore diameters was synthetized by a low-cost way. The pore size was controlled subtly by adjusting the ratio of benign solvent (water) and expansion inhibitor (ethanol). The analysis by FI-IR showed that phosphate group on the KGMP and CL-KGMPs molecules; SEM analysis indicated that when KGMP was cross-linked by sodium trimetaphosphate, its surface became uneven and brought out a little fold-like structure, specific surface increased significantly that was beneficial to the water retention capacity. Moreover, the best water retention capacity and swelling degree were observed when ethanol concentration was 45%. At the same time Q_T achieved its peak value, it was 5.686 mmol/g and superior to CM sephadex C-25 (4.5 mmol/g). And determining how to strengthen an application as an ion exchange material is next main work for us.

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References

Castellani, O., Martinet, V., David-Briand, E., Guerin-Dubiard, C. & Anton, M. (2003). Egg yolk phosvitin: Preparation of metal-free purified protein by fast protein liquid chromatography using aqueous solvents. *Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences*, *791*(1–2), 273–284.

Chen, L. G., Liu, Z. L., Chen, Y. J. & Zhuo, R. X. (2005). Synthesis and characterization of phosphated konjac glucomannan hydrogels. *Chinese Chemical Letters*, *16*(12), 1652–1654.

Duarte, M., Ferreira, M., Marvao, M. & Rocha, J. (2002). An optimised method to determine the degree of acetylation of chitin and chitosan by FTIR spectroscopy. *International Journal of Biological Macromolecules*, *31*(1–3), 1–8.

Focher, P. (1990). Alkaline N-deacetylation of chitin enhanced by flash treatments: Reaction kinetics and structure modifications. *Carbohydrate Polymers*, *12*(4), 405–418.

Li, B. & Xie, B. (2004). Synthesis and characterization of konjac glucomannan/poly(vinyl alcohol) interpenetrating polymer networks. *Journal of Applied Polymer Science*, *93*(6), 2775–2780.

Li, J., Zhang, X., Chen, J., Xia, J., Ma, M. & Li, B. (2009). Frontal polymerization synthesis and characterization of Konjac glucomannan–graft–acrylic acid polymers. *Journal of Polymer Science Part A: Polymer Chemistry*, *47*(13), 3391–3398.

Liu, M., Fan, J., Wang, K. & He, Z. (2008). Synthesis, characterization, and evaluation of phosphated cross-linked konjac glucomannan hydrogels for colon-targeted drug delivery. *Informa Healthcare*, *14*, 397–402.

Liu, Z. L., Hu, H. & Zhuo, R. X. (2004). Konjac glucomannan–graft–acrylic acid hydrogels containing azo crosslinker for colon-specific delivery. *Journal of Polymer Science. Part A: Polymer Chemistry*, *42*(17), 4370–4378.

Liu, J., Li, B., Zhu, B., Fu, R. H., Yuan, L. N., Huang, W., et al. (2010). Study on properties and aggregation structures of deacetylated konjac glucomannan/chitosan hydrochloride absorbent blend gel films. *Journal of Applied Polymer Science*, *115*(3), 1503–1509.

Masram, D. T., Bhave, N. S. & Kariya, K. P. (2010). Synthesis of resin IV: Salicylic acid, diaminonaphthalein, and formaldehyde terpolymer and its ion exchange. *Journal of Applied Polymer Science*, *117*(1), 315–321.

Peterson, E. & Sober, H. (1956). Chromatography of proteins. I. Cellulose ion-exchange adsorbents. *Journal of the American Chemical Society*, *78*(4), 751–755.

Tweeten, K. A. & Tweeten, T. N. (1986). Reversed-phase chromatography of proteins on resin-based wide-pore packings. *Journal of Chromatography A*, *359*, 111–119.

Wang, Y., Ye, Y., Li, B. & Xie, B. (2009). Dry preparation of konjac glucomannan phosphate ester with high degree of substitution. *Journal of Anhui Agricultural Science*, *37*(25), 12173–12175.