Journal of Applied Science and Engineering Innovation, Vol.7, No.1, 2020, pp. 44-48
ISSN (Print): 2331-9062
ISSN (Online): 2331-9070

Preparation of Carrageenan Aerogel from Extraction of *Chondrus* and Application in Oil/Organic Solvents Absorption

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Abstract: Carrageenan aerogel was prepared by freeze-dried technology from extraction of *Chondrus* with potassium chloride as cross-linking agent and it was used to absorb water, oils and organic solvents. The chemical structure and microstructure of the carrageenan and carrageenan aerogels were characterized by FTIR and SEM, It was found that the concentration of carrageenan solution had a significant effect on the microstructure and adsorption properties of aerogels. When the concentration of carrageenan increased from 1 wt% to 4 wt%, the pore size of aerogels increased obviously. When the carrageenan concentration increased from 1 wt% to 4 wt%, the maximum water absorption ratio of the aerogel decreased from 21.5 g/g to 11.5 g/g. At the carrageenan concentration of 2.5%, the oil absorption capacity was 20-25 times of its own weight, and the adsorption amount of the organic solvent also exceeded 14 g/g. As for soybean oil and DMF, the adsorption amount was maintained at 14-17 g between the second and tenth times, which showed that the carrageenan aerogels had a good adsorption stability and excellent cycle performance.

Keywords: Extraction, Carrageenan aerogel, Adsorption, Repetitive absorption rate

INTRODUCTION

With the rapid development of the social economy, resource shortage and environmental pollution have become important factors restricting the sustainable development of countries around the world. Therefore, biomass resources used as raw materials and green technology adopted to research and develop economy are becoming an important measure for countries around the world to achieve the goal of sustainable green development [Bi, *et. al*., 2015] [Ivar, *et. al*., 2014][Iwata, *et. al*., 2015].

Polysaccharides are a class of biopolymers extracted from plant or sea algae. They are rich in resources. Due to their biocompatibility, degradability and non-toxic, they have been used in various fields such as food, medicine, paper industry, etc.[Liu, *et. al*., 2015].They are also ideal raw materials for the preparation of organic aerogels in modern industrial applications. The development of plant polysaccharide aerogel conforms to the government's requirements for environmentally friendly materials and is a new direction for aerogel materials [Wang, *et. al*., 2017].

Many oil-absorbing materials such as expanded graphite and inorganic silicon aerogel have been reported in the literature [Hai, *et. al*., 2015][Liu, *et. al*., 2016],such oil-absorbing materials have good adsorption effects, but their high cost limits their wide application. There are also organic synthetic polymer materials, such as polyurethane [Wu, *et. al*., 2014], polystyrene foam materials [Lin, *et. al*., 2012]. Such oil-absorbing materials have good repeatability but poor biodegradability. Therefore, the natural and sustainable adsorption materials those are cheap and easy to obtain have become the hotspot of current research because of their remarkable characteristics such as renewable, biodegradable, high strength and environmental friendliness.

Carrageenan is a plant polysaccharide extracted from red algae and is a natural renewable material which is abundant in the ocean. It exhibits excellent gel properties and rheological properties. Due to the unique properties of carrageenan, such as no toxicity, ionic, thermotropic, chelating and encapsulating properties, it is an excellent choice as a food grade adsorbent [Genesan, *et. al*., 2014].

In this paper, carrageenan aerogels were prepared by freeze-drying method using a non-polluting and widely used carrageenan as raw material. The morphology and structure of the product were analyzed, and the aerogel oil absorption and organic solvent properties were tested.

EXPERIMENTAL METHOD

Materials and methods

Chondrus of class rhodophyceae (red algae) was collected in Dalian Bay, China during May and dried for later use. Commercial κ-carrageenan and ι-carrageenan were purchased from Qingdao juda ocean seaweed industry Co. LTD. Distilled water was purified, soybean oil, pump oil, sodium hydroxide, potassium chloride, absolute ethanol, dimethicone, cyclohexane, n-hexane, petroleum ether and dimethyl sulfoxide were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and those reagents were all analytical grade, commercially available, and used as received.

Preparation of carrageenan aerogel

The carrageenan solution was prepared from the *Chondrus* via a method described by Min Dong [Dong, *et. al*., 2018] with a slight modification. A certain amount of *Chondrus* was soaked in 7% sodium hydroxide aqueous solution for half an hour at a temperature of 75°Cto remove the pigment. Thereafter, the *Chondrus* was washed to be neutral, then, a proper amount of deionized water was added to the *Chondrus* and the water bath temperature was adjusted to 95°C for 2h.The extraction was filtered with two layers 200mesh gauze and then collected to be used as carrageenan solution.

Preparation of carrageenanaerogel (CAA): The carrageenan solution obtained above was divided into five portions and then diluted to a proper concentration (1wt%, 2wt%, 2.5wt%, 3wt%, 4wt%) with the volume of 10mL. The aqueous solution of potassium chloride was added dropwise to the carrageenan solution with stirring, and the temperature of the carrageenan solution was maintained at 90°C. And then the mixture was kept still and cooled to room temperature for aging. After 12 hours of aging, the hydrogel was obtained, and excess potassium chloride was washed with ethanol and then with water. Finally, the hydrogel was freeze-dried at 20 Pa after freezing in refrigerator to obtain the carrageenan aerogel (CAA). And the CAA was heated in the oven with the temperature of 110℃ for about 24h and stored for use.

Characterization of carrageenan and carrageenan aerogel

The chemical structure of carrageenan was characterized by an infrared spectrometer (Nicolet 5700, American Thermoelectric Company). The carrageenan and KBr were mixed in a mortar and ground uniformly, and pressed into a thin sheet for testing; the scanning range was 4000-400 cm^{-1}, and the resolution was 4 cm^{-1}.

Scanning electron microscope (Hitachi TM-3000, Japan) was used to observe the microstructure of carrageenan aerogel. Morphology analysis was performed on the samples after gold plating at an acceleration voltage of 3 kV.

Ignoring the air density inside the aerogel, the porosity of the carrageenan aerogel is calculated according to the following formula (1):

$$P(\%) = (1 - \frac{\rho_b}{\rho_s}) \times 100\% \quad (1)$$

Where ρ_b is the bulk density of carrageenan aerogel, it can be obtained from the ratio of the mass to the volume; ρ_s (1.72g cm^{-3}) is the density of carrageenan skeleton[Genesan, *et. al*., 2014].

Carrageenan aerogel pore volume (V_P) is calculated from the aerogel after water absorption. Water penetrates the pores of the sample, so V_p can be calculated according to the following formula (2) [Li, *et. al*.,2014]:

$$V_p = \frac{M_{wet} - M_{dry}}{\rho M_{dry}} \quad (2)$$

M_{wet} is the quality of the sample completely immersed in water until the swelling equilibrium reached; M_{dry} is quality of the freeze-dried sample; ρ (0.997 g cm^{-3}, 25 ° C) is the density of water. Three replicates were tested for each set of samples.

The water absorption ratio (R) was calculated according to the following formula (3) [Zhou, *et. al*., 2007]:

$$R = (M_1 - M_0) / M_0 \quad (3)$$

Accurately weighed a certain amount of carrageenan aerogel (M_0), put it into 50 ml deionized water, after a certain minute, remove the CAA of the water, absorb excess water on the surface of CAA with a wipe paper and recorded its weight (M_1).

The maximum absorption rate (C_m) of CAA for oils/organic solvents according to formula (4) [Nguyen, et. al., 2013]:

$$C_m(g \cdot g^{-1}) = \frac{W - W_0}{W_0} \quad (4)$$

Accurately weigh a certain amount of CAAs (W_0), and then put the CAAs into the beaker with 25ml oils organic solvents (vegetable oil, pump oil, dimethicone, Cyclohexane, n-hexane, petroleum ether, DMSO and DMF). After adsorption equilibrium, remove the CAAs, and let them drip freely for 30 seconds, and then weigh the CAAs and record their weights (W).

The recycled property of the CAA was estimated with the absorption/extrusion experiment. The CAA absorbed the oil (or organic solvent) and squeezed after oil (or organic solvent) absorption

RESULTS AND DISCUSSION

Characterization of carrageenan and carrageenan aerogel

Figure 1 was the FTIR spectrum of carrageenan. There was the basic structural groups of carrageenan: telescopic vibration of C-H on the C-6 ring of molecular skeleton (2900cm^{-1}), extensible vibration of hydroxyl groups in the molecular structure of carrageenan (3400cm^{-1}), the stretching vibration of the 3,6-galactoside group (930cm^{-1}), bending vibration of D-galactose-sulfate group (840cm^{-1}). The sulfate group is a special group of carrageenan whose bending vibration occurred at a wavelength of 1250cm^{-1}, there was also a C-O-C group (1100 cm^{-1}) and a methylene group (1460 cm^{-1}) linked to oxygen in the structure. In addition, carrageenan powder and ι-carrageenan powder prepared from the extraction showed obvious characteristic peaks around 810 cm^{-1}. It indicated the presence of sulfate groups at the C-2. Anhydro-D-galactose residue (DA2S) is a characteristic band of ι-carrageenan [Pereira, *et. al*., 2009] [Pereira, *et. al*., 2003]. Therefore, we inferred that the carrageenan powder extracted from *Chondrus* was mainly ι-carrageenan.

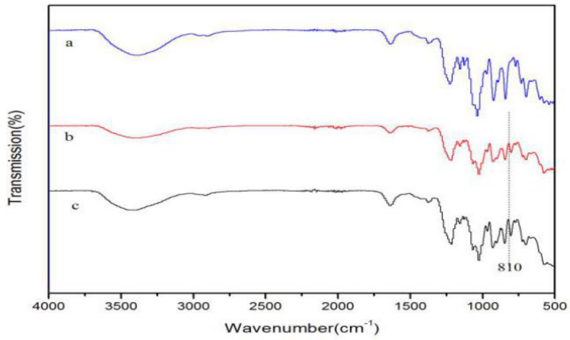

Figure1. FTIR spectrum of carrageenan((a). Commercial κ-carrageenan;(b). Carrageenan extracted from *Chondrus*; (c). Commercial ι-carrageenan)

The morphology of different carrageenan concentrations of the fracture surface of CAA was shown in Figure 2. The SEM image showed that a distinct interconnected three-dimensional network structure in the aerogel. Moreover, aerogels at concentrations of 1 wt%, 2 wt%, 2.5 wt%, 3 wt%, and 4 wt% exhibited different hierarchical porous structures due to the difference in carrageenan concentration. The network structure of CAA with 1wt% and 2wt% concentration is incomplete. With the increase of carrageenan concentration, the pore size of the aerogel also increased and the pore structure became more regular. This may be due to the increase in carrageenan concentration, the carrageenan molecules easily to aggregate to form a large pore-like structure.

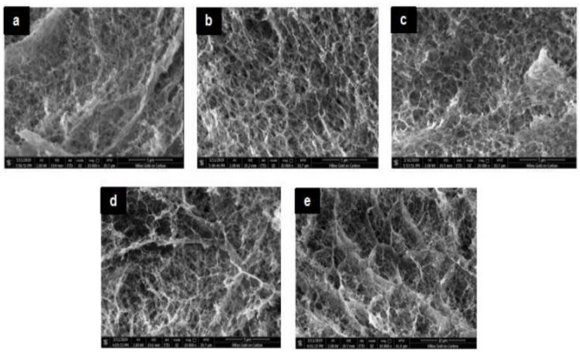

Figure 2. Scanning electron microscopy images of the fractured surface of carrageenan aerogels with concentrations of (a) 1 wt%, (b) 2 wt%, (c) 2.5wt%, (d) 3 wt%, (e) 4 wt%

In order to further study the effect of carrageenan concentration on the aerogel microstructure, the density (ρ_b), pore volume (V_p) and porosity (P) of carrageenan aerogels were determined. The results were shown in Table 1. The CAA with the carrageenan concentration of 1wt% had a density of only 0.16 g/cm^3, but the porosity and pore volume were 90.7% and 21.5 cm^3/g, respectively. When the carrageenan concentration was increased from 1 wt% to 4 wt%, the density of the aerogel gradually increased, and the porosity and pore volume gradually decrease. However, the porosity of the 4 wt% carrageenan aerogel still exceeded 87%.

Table 1 Density, pore volume and porosity of carrageenan aerogel

Sample	ρ_b (g/cm^3)	V_p (cm^3/g)	P（%）
1%CAA	0.16	21.50	90.70
2%CAA	0.16	20.50	90.40
2.5%CAA	0.17	16.51	90.10
3%CAA	0.18	15.10	89.53
4%CAA	0.21	11.52	87.79

Figure 3 was the relationship between water absorption ratio and absorption time of carrageenan aerogels with different carrageenan concentrations. It can be seen that the water absorption and swelling balance of carrageenan can be quickly reached in about 20 minutes. When the concentration of carrageenan increased from 1 wt% to 4 wt%, The maximum water absorption of carrageenan aerogel decreased from 21.5 g / g to 11.5 g / g.

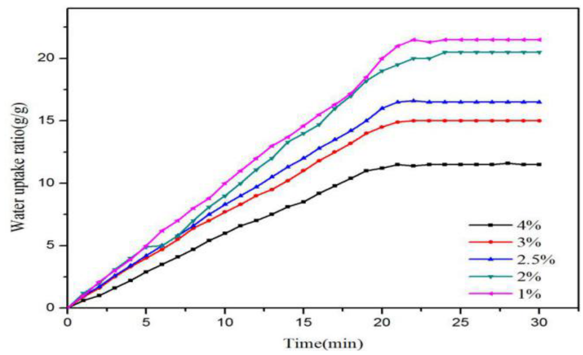

Figure 3. Relationship between water absorption ratio and absorption time of carrageenan aerogels with different carrageenan concentrations

Carrageenan aerogel with carrageenan concentration of 2.5wt% was used to absorb the oils/organic solvents including vegetable oil, pump oil, dimethicone, cyclohexane, n-hexane, petroleum ether, DMSO and DMF in this study. Figure 4 was the oils/organic solvents absorption capacity of carrageenan aerogel with 2.5wt% carrageenan concentration. The adsorption amount of vegetable oil, pump oil and dimethicone was 23.6, 20.73 and 19.57g/g, respectively. At the same time, the adsorption amount for cyclo-hexane, n-hexane, petroleum ether, DMSO and DMF was also exceeded 14 g/g. Compared with other polymer oil-absorbing materials that have been reported, such as rice straw material (9.71g/g) [Jin, *et. al*.,2015], oil-absorbing plant polysaccharide aerogel (12-22g/g), (12-22g/g) [Jin, etc. Choi, *et. al*., 2011], polydimethyl siloxane sponge (4-11g/g) [Liao, *et. al*.]. Carrageenan aerogel exhibited a high adsorption capacity. The difference in absorption capacity for different oils and organic solvents may be due to the characteristics of the aerogel surface and the nature of the liquid (density, surface tension and hydrophobicity) [Li, *et. al*.,2014].

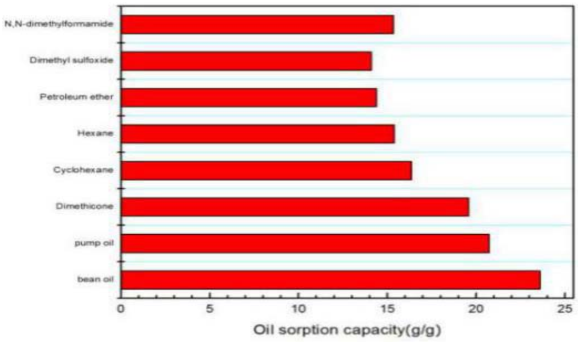

Figure 4. Organic solvents absorption capacity of carrageenan aerogel with 2.5wt% carrageenan concentration

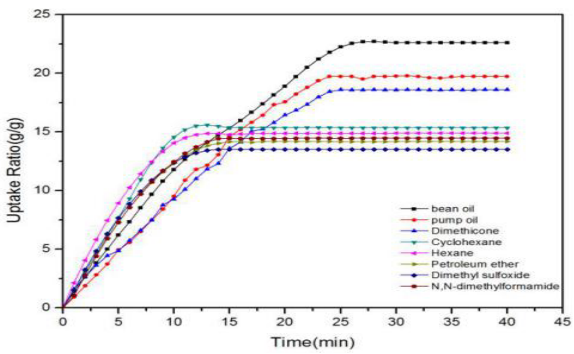

Figure 5. Absorption equilibrium curve of carrageenan aerogel in different oils/organic solvents

Figure 5 was the absorption equilibrium curve of carrageenan aerogel in different oils/organic solvents. During the absorption process, the liquid can quickly penetrate into the interpenetrating porous structure of the carrageenan aerogel, and the absorption equilibrium can be quickly reached. For low viscosity organic solvents: cyclohexane, n-hexane, petroleum ether, DMSO and DMF, the absorption equilibrium can be achieved within 10 minutes, and the absorption equilibrium can be reached within 20 minutes for high viscosity organic solvents: vegetable oil, pump oil and dimethicone.

The carrageenan aerogel can be used to absorb the oils and organic solvents recycling by simple extrusion method for its good mechanical properties and elasticity. As shown in Figure 6, 1 g carrageenan aerogels with the carrageenan concentration of 2.5% filled with vegetable oil was simply squeezed, and the vegetable oil inside was squeezed out to collect and recycle. The first absorption of vegetable oil to a saturated mass of 23.86g/g, through five adsorption extrusion cycles, the adsorption amount dropped to 17.98g/g. This was because the vegetable oil remained in the internal voids of the aerogel and the high viscosity oil cannot be completely removed by direct extrusion. Similarly, in Figure 7, for DMF, after five cycles of adsorption and extrusion, from 12.30g/g to 11.05g/g, the absorption capacity still reached the 89.6%. As for vegetable oil and DMF, the absorption amount between the second and tenth times was maintained at 11.00-16.00 g/g, it showed a good adsorption stability and excellent cycle performance. Therefore, the carrageenan aerogel is a potential material in dealing with various oil and organic solvent leakage.

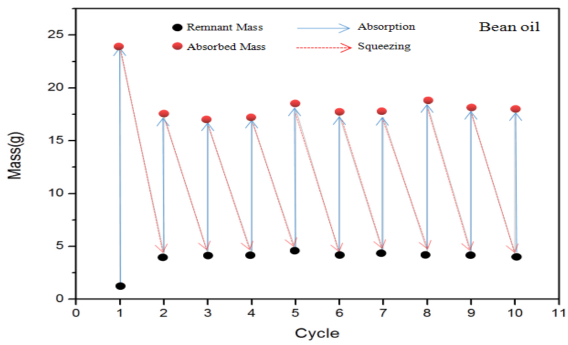

Figure 6. Repeated absorption of oil by aerogel

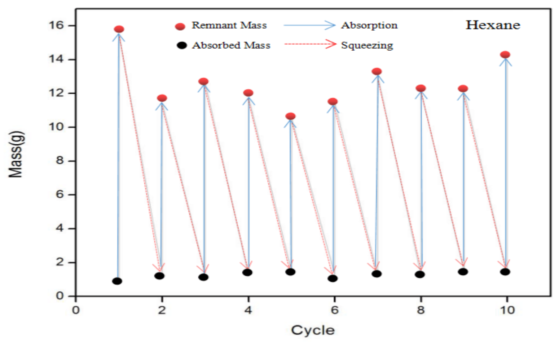

Figure 7. Repeated absorption of DMF by carrageenan aerogel

CONCLUSION

In this paper, a simple, green method was used to prepare carrageenan aerogel with carrageenan extraction from *Chondrus*and potassium chloride. The carrageenan aerogel is charaterized with low density, high porosity and high water and oils/organic solvents absorption capacity. When the concentration of carrageenan increased from 1 wt% to 4 wt%, the pore size, the maximum water absorption ratio of the carrageenan aerogel decreased from 21.5 g/g to 11.5

g/g. When the carrageenan concentration is 2.5%, the oil absorption capacity can absorb water 20-25 times of its own weight, and the absorption amount of the organic solvent also exceeds 14 g/g. For soybean oil and DMF, the adsorption amount between the second and tenth time was maintained at 14-17g. The results showed that the carrageenan aerogel had a good absorption stability and excellent cycle performance in oils/organic solvents absorption. Therefore, carrageenan aerogel is an efficient and environmentally friendly material for adsorbing oils and organic solvents.

ACKNOWLEDGMENTS

This work was supported bythe National Natural Science Foundation of China (50803030), the Postdoctoral Science Special Foundation of China (201104581), the Postdoctoral Science Foundation of China (20100471495).

REFERENCES

Bi Gong-bing, LUO Yan, DING Jing-jing, etc. Environmental performance analysis of Chinese industry from a slacks-based perspective [J]. Annals of Operations Research, 2015, 228(1): 65-80.

ChoiS J, KWON T H, Im H,et a1. A polydimethyl siloxane (PDMS)sponge for the selective absorption of oil from water [J]. ACS Applied Materials & Interfaces, 2011, 3(12):4552-4556.

Dong Min, XUE Zhi-xin, LIU Jing-jing, etc. Preparation of carrageenan fibers with extraction of *chondrus* via wet spinning process [J]. Carbohydrate Polymers, 2018, 194, 217–224.

Kathirvel Ganesan, LORENZ Ratke. Facile preparation of monolithic κ-carrageenan aerogels [J]. Soft Matter, 2014, 10.

Hai Jin. Preparation and properties of oil-absorbing materials based on corn straw [D]. Harbin Institute of Technology, 2015.

Ivar do Sul J A, COST M F. The present and future of microplastic pollution in the marine environment [J]. Environmental Pollution, 2014, 185: 352-364.

Iwata Tadahisa. Biodegradable and bio-based polymers: future prospects of eco-friendly plastics [J]. Angewandte Chemie International Edition, 2015, 54(11):3210-3215.

Jin Chun-de, HAN Sheng-jie, LI Jing-peng, etc. Fabrication of cellulose - based aerogels from waste newspaper without any pretreatment and their use for absorbents [J]. Carbohydrate Polymers, 2015, 123: 150-156.

Liao Qian. Preparation of functional cellulose aerogel and its application in water purification [D].

Liu Hong-zhi, CHEN Yu-fei, Yan An, etc. Research progress of cellulose-based aerogel oil-absorbing materials [J]. Journal of Polymer Science, 2016(5): 545-559.

Lin Jin-you, SHANG Yan-wei, DING Bin, etc. Nanoporous polystyrene fibers for oil spill cleanup [J]. Marine Pollution Bulletin, 2012, 64(2): 347-352.

Liu Jun, WILLFÖR S, XU Chun-lin. A review of bioactive plant polysaccharides: biological activities, functionalization and biomedical applications [J]. Bioactive Carbohydrates and Dietary Fibre, 2015, 5(1):31-61.

Li Wei , WU Yue-han , LIANG Wei-wei, etc. Reduction of the Water Wettability of Cellulose Film through Controlled Heterogeneous Modification [J]. ACS Applied Materials & Interfaces, 2014, 6(8):5726-5734.

Li Yu-wei. Testing of Limiting Oxygen Index and Influencing Factors [J]. Science & Technology Information, 2014, 12(20): 224.

Nguyen Son T, FENG Jing-duo, Le Nhat T, etc. Cellulose Aerogel from Paper Waste for Crude Oil Spill Cleaning [J]. Industrial & Engineering Chemistry Research, 2013, 52(51):18386-18391.

Pereiar L, AMADO A M, CRITCHLEY A T, etc. Identification of selected seaweed polysaccharides (phycocolloids) by vibrational spectroscopy (FTIR-ATR and FT-Raman) [J]. Food Hydrocolloids, 2009, 23(7): 1903-1909.

Pereira L, SOUSA A, COELHO H, etc. Use of FTIR, FT-Raman and 13C-NMR spectroscopy for identification of some seaweed phycocolloids [J]. Biomolecular Engineering, 2003, 20(4): 223-228.

Wang Lei, LIU Chang-jian. Preparation of oil-absorbing materials by rice straw hydrothermal treatment-transesterification modification [J]. Chemical Industry and Engineering Progress, 2017(5):1811-1817

Wang Yixin, CHEN Wei, YAN Ying, etc. Research Progress in the Application of Plant Polysaccharide Aerogel Materials [J]. Journal of Wuhan University of Technology, 2017(5): 443-449

Wu Da-xiong, WU Wen-juan, YU Zi-ya, etc. Facile Preparation and Characterization of Modified Polyurethane Sponge for Oil Absorption[J]. Industrial & Engineering Chemistry Research, 2014, 53(52):20139-20144.

Zhou Jin-ping, CHANG Chun-yu, ZHANG Ru-ping, etc. Hydrogels prepared from unsubstituted cellulose in NaOH/urea aqueous solution [J]. Macromolecular Bioscience, 2007, 7(6): 804-809.