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SPECIALTY SECTION

This article was submitted to Polymeric and Composite Materials, a section of the journal Frontiers in Materials

RECEIVED 08 November 2022 ACCEPTED 01 December 2022 PUBLISHED 14 December 2022

CITATION

Lu H, Jiang X, Wang J and Hu R (2022), Degradable composite aerogel with excellent water-absorption for trace water removal in oil and oil-in-water emulsion filtration. *Front. Mater.* 9:1093164. doi: 10.3389/fmats.2022.1093164

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Degradable composite aerogel with excellent water-absorption for trace water removal in oil and oil-in-water emulsion filtration

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In this study, using chitosan (CS) and carboxymethyl cellulose (CMC) as backbone and introducing citric acid (CA)to enhance the electrostatic interaction of the system, citric acid/chitosan/carboxymethyl cellulose (CA/CS/CMC) aerogel is obtained by simple freeze-drying. CA/CS/CMC composite aerogel exhibits light weight, low density, high porosity, outstanding hydrophilic and water retention properties, and satisfactory underwater oleophobicity. The water adsorption capacity of the obtained aerogels can reach 43.87-80.28 g/g, which are far more than that of carboxymethyl cellulose and chitosan aerogels (14.27-20.08 g/g). In addition, with strong hydrophilicity, underwater oleophobicity and water retention endowed by the rough internal microstructure and the rich hydroxyl, amino, and carboxyl groups, the fabricated aerogel can also be used as a filter to achieve effective separation of oil-inwater emulsions and oil/water mixtures. The separation efficiency of aerogel for oil/ water mixtures are higher than 90.7%. Because the developed preparation method is green, simple and mild and the raw materials are readily available and environmentally friendly, the obtained CA/CS/CMC aerogel with strong water absorption capacity and good separation efficiency displays a promising application in water-oil separation.

KEYWORDS

chitosan, carboxymethyl cellulose, water absorption (A), water retention, aerogel, emulsion separation

1 Introduction

The constant happening of crude oil leakage incidents, coupled with the massive discharge of oily wastewater in people's daily life and industry, will cause huge pollution to the environment and seriously threaten human health and economic development (Li et al., 2018; Zhong et al., 2021; Chen et al., 2014; Franco et al., 2014). The application of filter paper (Li et al., 2019; Cheng et al., 2018), membrane (Zhong et al., 2021; Wu et al., 2022) and aerogel (Korhonen et al., 2011; Laitinen et al., 2017) in water-oil separation has also been reported. Currently, one of most effective methods is separating oil and water using physical adsorption

of porous materials, which is also inexpensive, environmentally friendly and easy-operated (Korhonen et al., 2011; Laitinen et al., 2017; Saleem et al., 2018). In the early 1930s, a new type of material, aerogel, was proposed by Kistler (Kistler, 1931) Aerogel is obtained by replacing liquid medium of gel with gaseous medium with no significant changing its internal structure. Aerogel has many excellent characteristics, like light weight, abundant pores, and extremely strong adsorption. At present, it has been widely applicated in aerospace (Jones, 2006), thermal insulation (Shi et al., 2013; Takeshita and Yoda, 2015), adsorption materials (Huang and Shi, 2014), drug loading (Işıklan et al., 2011) and other fields. Aerogel is also ideal material for liquid absorption and storage due to their porous nature. The research directions of the aerogels for water-oil separation are divided mainly into two types: one is to improve hydrophobicity and oil-absorbing properties of aerogels by impregnation, solvent exchange, atomic layer deposition, gelation (Yang et al., 2020), and then the good water-oil separation effect will be produced (Han et al., 2016; Wan et al., 2015; Cao et al., 2015; Akhlamadi and Goharshadi, 2021; Wang and Liu, 2019). However, due to the lipophilic nature of this aerogel, oil can easily stick to the aerogel or even get blocked by the oil, resulting in contamination of the material. In addition, the adsorbed oil cannot be cleaned away, which will increase the difficulty of oil recovery and the risk of secondary pollution in post-processing. High density of water also can form a water barrier that hinders the gravity-driven separation process (Zhang et al., 2013). The other direction is to use the hydrophilicity of aerogels to realize water-oil separation and no hydrophobic modification is performed. For instance, Sun et al. found that superabsorbent fibers can absorb 10-50 times their own weight of ordinary tap water (Sun, 2008). This kind of annular filter made of fibers can allow the passage of water and block oil particles with smaller diameters, so as to achieve the good water-oil separation. This material with superhydrophilic and underwater superoleophobic characteristics is able to solve the problem of low separation efficiency caused by water barrier and the problem of pores blocking of the hydrophobic materials (Wang et al., 2020). Thus, this material with hydrophilic/oleophobic properties provides a viable alternative for water-oil separation (Zhang et al., 2020).

Nowadays, there are numerous studies on the preparation of hydrophilic/oleophobic materials by constructing nano/micro-scale structures and introducing appropriate chemicals. However, most reported materials have intolerant surfaces and poor water retention ability (Yuan et al., 2017; Ge et al., 2018; Xu et al., 2018; Koh et al., 2019; Zhang et al., 2020), which is unfavorable for stable separation properties. Specially, the multi-scale topography is customarily in need of complex manufacturing course, which sets a limit for practicability of this materials. Hydrophilic aerogels can be obtained from hydrogels by appropriate drying methods. For instance, Liu et al. synthesized chitosan/lithium sulfonate hydrogel by electron beam irradiation, and obtained an aerogel with porous structure and CO_2 capture ability by freeze-drying (Liu et al., 2021); He et al. prepared a multifunctional polyimide (PI) aerogel adsorbent from poly(amic acid) ammonium salt (PAS) hydrogel by freeze-



drying (He et al., 2017). Carboxymethyl cellulose (CMC) is rich in hydrophilic groups like carboxyl and hydroxyl groups (Kono et al., 2016; Xiang et al., 2018), and it is an anionic polysaccharide. The molecular chain of chitosan (CS) also has many hydroxyl and amino groups (Guibal et al., 2014; Rajoka et al., 2019; Cheung et al., 2015), and it is a natural biodegradable cationic polymer. Due to the existence of abundant polar hydrophilic groups, CMC and CS are suitable for developing composite hydrogels based on natural biopolymers. The two materials have the advantages of nonpolluting, abundant sources, low cost, biodegradability and biocompatibility (Uyanga et al., 2020).

In this study, composite aerogels were synthesized by using CS and CMC as the double-polymer aerogel framework and introducing CA to enhance the electrostatic interaction of the system. The detailed goals of this study are to (a) synthesize environmentally sustainable ion cross-linked CA/CS/CMC composite aerogel with good underwater oleophobicity and strong water absorption and evaluate the effect of changing the content of two raw materials on the performances of the aerogel; (b) evaluate the oil/water separation property of fabricated aerogel. The studies show CA/CS/CMC composite aerogel with strong water absorption-retention properties and good oil/water separation effect has promising applications in oil-polluted water and oil-in-water emulsions.



2 Experimental

2.1 Materials

Carboxymethyl cellulose III (CMC) (M.W. 250000, DS = 0.9, 1,500–3,100 mPa s) was obtained from Shanghai Macklin Biochemical Co., Ltd. Chitosan (CS) (BR grade) was acquired from Shanghai Sinopharm Chemical Reagent Co., Ltd. The rest of the chemical reagents were acquired from Shanghai Sinopharm Chemical Reagent Co., Ltd. and all are AR grade.

All chemicals were used as received without further purification.

2.2 Preparation of CA/CS/CMC composite aerogels

An appropriate amount of CS powder was added to 1% acetic acid solution (v/v) and stirred at room temperature to obtain 0.5wt%, 1wt%, 1.5wt%, 2wt%, 2.5wt%, 3wt%, 3.5wt%



and 4wt% the CS solution. An appropriate amount of CMC powder was added to deionized water and stirred at 80°C to obtain 0.5wt%, 1wt%, 1.5wt%, 2wt%, 2.5wt%, 3wt%, 3.5wt% and 4wt% CMC solutions. In room temperature, after mixing the same volume of CS solution and CMC solution evenly, added CA (15% of CS mass), stirred until completely dissolved, and maintained at -18°C for at least 6 h. CA/CS/CMC composite aerogels were obtained by freeze-drying for 48 h. CA/CS/CMC composite aerogels' names are determined by the mass fraction of raw material solution. For instance, the raw material solution used to synthesize S₁M₁A aerogel is 1 wt% CS and 1 wt% CMC. (Supplementary Tables S1, S2).

2.3 Characterizations

The sample was thoroughly dried, mixed with potassium bromide (KBr) powder and ground into powder, and Fourier Transform infrared spectrum was tested (Nicolet 6,700, American Thermo Electron Co., Ltd.). The internal microstructure of composite aerogels was detected by scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) (JSM-5510LV, JEOL Ltd.). Liquid contact angle (CA) was determined by means of CA measuring device (DSA100, Germany Kruss Ltd.). The water droplet and chloroform droplet for CA measurements were $5 \,\mu$ L and 20 μ L, respectively. The compressive strength of the aerogel was measured by an electronic universal testing machine (CMT, MTS System Ltd.).

2.4 Apparent densities and porosities

The diameter (*D*) and height (*H*) of the sample was measured with a vernier caliper, the mass (*m*) of the sample was tested with an electronic balance, and the apparent density (ρ_b) of the aerogel is determined by Eq. 1. The automatic true density analyzer (3H-2000TDI, Beijing Beishide Instrument Technology Co., Ltd.) was applied to measure the true density (ρ_s) of the sample, and the aerogel porosity (*P*) can be measured by using Eq. 2.

$$\rho_b = \frac{m}{\frac{\pi}{4}D^2H} \tag{1}$$

$$\boldsymbol{P} = \left(1 - \frac{\rho_b}{\rho s}\right) \times 100\% \tag{2}$$

2.5 Adsorption properties and oil-water separation experiment

The sample (m_0) was put into a beaker containing deionized water or an organic solvent. After a certain interval, the sample was taken out and drained for 2s, the mass (m) was measured.

The adsorption rate (*C*) of deionized water or organic solvent by aerogel was calculated by Eq. 3.

$$C = \frac{m - m_0}{m_0} \tag{3}$$

The oil was poured into deionized water (20% v/v) and stirred (600 rpm/min) at least 15 h to get the oil-in-water emulsion. Oil-water mixture (20% v/v) was prepared by simply mixing deionized water with oil. Optical microscope (OM) (BK6000, Chongqing Auto Optical Instrument Co., Ltd.) was used to observe oil-in-water emulsions, oil/water mixtures, and filtrates.

After sample was put into the funnel and saturated with deionized water, a certain volume (V_0) of oil/water mixture and (oil density< 1) was poured into the funnel and the oil will be blocked on the aerogel. The volume (V) of the remaining oil was measured after the water is completely filtered. Each sample should be measured at least 3 times and averaged. The water-oil separation efficiency (R) of aerogel was calculated by Eq. 4.



$$\boldsymbol{R} = \frac{\boldsymbol{V}}{\boldsymbol{V}_0} \times 100\% \tag{4}$$

3 Results and discussion

3.1 Preparation and wettability

Ion-crosslinking CA/CS/CMC composite aerogel was prepared using CMC, CS with high hydroscopicity and moisture retention as the matrix and introducing CA. Figure 1A shows illustration for the manufacturing procedure of CA/CS/CMC composite aerogel. To study the wettability of CA/CS/CMC composite aerogel, the contact angle was measured. Figures 1B,C show the water wetting behavior in air and oil wetting behavior underwater of CA/CS/CMC composite aerogels. In air, when the water droplet drops on aerogel's surface, the strong hydrophilicity makes the water droplet be completely absorbed by CA/CS/CMC composite aerogel within 2.272s, and the water CA is 0°. This is ascribed to the internal microstructure and the eminently abundant hydroxyl, amino, and carboxyl groups contained (Wang et al., 2020). When chloroform droplet was dropped on the aerogel's surface under water, it presents the underwater CA of $137.7 \pm 1.7^{\circ}$ on the aerogel surface, which was attributed to the porous structure inside the aerogel and hydrated form of polar groups (Zhang et al., 2020). The water wetting behavior in aerogel pores and oil-rejection behavior was displayed. When the surrounding atmosphere is air, the hydrophilicity of the CA/CS/CMC composite aerogel coupled with the porous nature allows water to continuously penetrate the aerogel (Figure 1D). Before oil-water separation, CA/CS/ CMC composite aerogel was completely wetted by water, causing its rough structure to be flooded by a major expenditure of water, and the repulsion between water and oil would prevent the aerogel from being contaminated by oil (Figure 1E) (Wang et al., 2020).



3.2 Morphology, structure, apparent density, and porosity

As can be seen from SEM images of CA/CS/CMC composite aerogels developed at different mass concentration (Figures 2A–H), it is clear that the CA/CS/CMC composite aerogel framework is mainly comprised of stacking of secondary sheet-like layers. And through the EDS point scanning spectrums of aerogel, it can be seen that there are C, N and O elements on the surface of aerogel with different mass concentration (Supplementary Figure S1). As the increase of CS/CMC total mass from 0.5 wt% to 4 wt%, the lamellae become



more regular, which also makes the maximum compressive strength of aerogels increase gradually at 60% strain (Supplementary Figure S2). There are a large number of nonuniform pores among the lamellae, which is as a result of the construction of multiple ice crystals when the solvent is frozen below the freezing point at low temperature. The dispersibility of CS and CMC in water is different (Ma et al., 2021), which affects the growth of ice crystals. After the ice crystals are sublimated into gas under vacuum conditions, uneven pores will be formed. The large number of folds not only increases the surface roughness of the composite aerogel, but also makes the



aerogel ultralight (Xu et al., 2020). Such rough surface and CS/CMC has an excellent affinity for water, which enable the aerogel to have excellent hydrophilicity and underwater oleophobicity (Padaki et al., 2015; Yue et al., 2019; Wang et al., 2020).

Figure 3A displays the FT-IR spectra of CMC, CS and $S_1M_1A.It$ can be seen from the figure that the characteristic absorption peaks of both CS and CMC are displayed in the infrared image of the composite aerogel, and the peak intensity of S_1M_1A is obviously stronger than that of the two raw materials. All three samples have broad absorption peaks at $3,700 \text{ cm}^{-1}$. The peak of CMC is attributed to the O-H stretching vibration, while CS and composite aerogels show this peak in addition to the effect of the above bond, as well as the role of N-H stretching vibration. Although it is superimposed by the broad absorption peak at 1581 cm^{-1} , it can still be seen that a new peak belonging to NH₃⁺ appears at 1633 cm^{-1} (Yong et al., 2002; De Vasconcelos et al., 2006;



Ostrowska-Czubenko et al., 2009). The peaks at 1581cm^{-1} and 1405cm^{-1} belong to the symmetrical and antisymmetric stretching vibrations of [O-C=O]⁻. The strong infrared absorption peaks at these two places prove that S_1M_1A is rich in carboxyl groups (Yong et al., 2002; De Vasconcelos et al., 2006). These results suggest that CMC, CS and CA are bound together by electrostatic interactions. Overall, a plentiful of hydrophilic functional groups including hydroxyl, amino, and carboxyl groups exist in S_1M_1A , which will contribute to the efficient adsorption of water molecules. The FTIR images of composite aerogels obtained at different raw material ratios (Figure 3B) shows that the absorption peak of S_1M_1A is significantly stronger than that of other aerogels, which was more conducive to water absorption.

Light weight and porous structure are essential characteristics of aerogels (Padaki et al., 2015; Yue et al., 2019). The apparent density and porosity of the material can directly reflect these two characteristics. As can be seen from the variation trends of the apparent density and porosity of the aerogel with different mass concentration, the apparent density of the prepared aerogels are within the scope of 0.0083–0.0636 g/cm³ and the porosity is above

96% (Figure 4). The two indicators prove that the fabricated aerogels are low-density porous material. As the increase of CS and CMS content in the system, the apparent density of the aerogel shows increasing trend. The results can be given explanatory notes by the fact that, at a same volume, the distance between polymer molecules decreases with the increase in the overall content of the feedstock, resulting in a decrease in porosity. Although the porosity of the aerogel decreases with the increase in the overall content of the feedstock, the lowest porosity still reaches above 96%. The porosity of aerogels is crucial for separation performance without any external force. The high porosity ensures that the gravity-driven water penetration can be achieved by the aerogel, and the separation process is fast and efficient (Wang et al., 2020).

3.3 Adsorption capacity and solvent retention performance

In the kinetics curves of water adsorption (Figures 5A,B), the water adsorption capacity of CA/CS/CMC aerogel reach about 18.17-64.64 g/g within 1 s, showing strong



hydrophilicity. The adsorption reaches saturation in 30 s. This suggests that the aerogel has a fast water absorption ability due to the high porosity and the abundant hydrophilic groups (Jia et al., 2018). In general, the water absorption rates of all different formulations of aerogels increase significantly at first and then decrease with prolonging time. Because polymer molecules were not fully stretched in water at the beginning. With the increase of time, water molecules fill the aerogel pores due to existence of capillary force among pores and abundant hydrophilic group in aerogel, and the water adsorption will finally reach saturation. Figure 5C displays the sorption kinetics of S₁M₁A for the organic solvents. The test results show that S1M1A can reach adsorption saturation within 1 s for five organic solvents, including ethanol, methanol, acetone, toluene, and chloroform. The water absorption capacity of aerogels with different formulations is shown in Figure 6A, B. It can be seen that the water absorption capacity of CA/CS/CMC composite aerogels firstly increases and then decreases. S1M1A has a maximum absorption capacity of 80.67 g/g. This is mainly because the

hydrophilic groups (hydroxyl, amino, and carboxyl groups) in S₁M₁A are exceedingly abundant. Increasing the total mass of CS and CMC will cause the decrease of the distance among polymer molecules and the porosity, resulting in the decrease of water absorption capacity (Yuan et al., 2016). Figure 6C shows that the adsorption capacities of S1M1A for different organic solvents are about 27-44 g/g. For methanol, acetone and toluene, the adsorption capacities are all around 27.15 g/g; for chloroform, the adsorption capacity is 44.81 g/g. The highest adsorption capacity for chloroform is due to the large density. As can be seen from the comparison of the as-prepared aerogels and several reported water absorbents, the water absorption capacity of CA/CS/CMC aerogel is far higher than that of other absorption materials (Table 1). Figure 7A shows the retention properties of S1M1A for water, ethanol, methanol, acetone, toluene, and chloroform. The aerogels saturated with organic solvents have obvious quality changes after 16 min. For chloroform, the obvious quality change can be found after 1 min. The quality of aerogels saturated with water deceases after 120 min and decreases sharply after 180 min. Moreover, the organic solvent in the aerogel volatilized completely in 32-120 min, but the volatilization of water needs to spend 2,880 min. This is because the prepared aerogels have abundant hydrophilic groups, which results in better water retention than organic solvents retention. Figure 7B is the picture of the aerogel before and after water absorption, which shows that the aerogel is hydrogel-like after absorbing water. The waterabsorbing aerogel still can float on the water surface after reaching adsorption saturation (Figure 7C), which is because of the low density and high porosity of the aerogel.

3.4 Oil/water separation ability

For purpose of evaluating the separation ability of CA/CS/ CMC aerogels to water on oil, the aerogel fully absorbed water and reached saturation before separation. Small amounts of methylene blue-stained water, coffee, milk, and tea on chloroform surface were fully absorbed by the water-wetted composite aerogel within several seconds, and no obvious residual liquid was found on the chloroform in the beaker (Figure 8). This indicates that CA/CS/CMC composite aerogel has remarkable separation ability for water-oil mixtures (Wang et al., 2015).

The oil/water separation process is shown in Figure 9A. When oil gets in touch with the water-saturated aerogel, an oil/ water/solid three-phase interface will be generated. Formation of the hydrated shell, coupled with water-oil incompatibility, can tremendously diminish the range of oil in direct contact with solid surfaces. Thus, water flows out from the lower end through the aerogel under the influence of gravity and oil is blocked in the upper layer, causing the good separation effect

Sorbents	Preparation	Porosity	Water absorption	References
Chitosan/polybenzoxazine/clay mixed matrix composite aerogel	Simple mixing, freeze drying	>93%	29 g/g	Alhwaige et al. (2020)
Alginate aerogel	Sol-gel method, supercritical drying	-	20 g/g	Mallepally et al. (2013)
Lignocellulosic aerogel	Sol-gel method	-	8.45 g/g	Wu et al. (2020)
2D nanofiber membrane	Electrospinning	-	5.14 g/g	Yuan et al. (2016)
3D nanofiber aerogel	Electrospinning, homogeneous dispersion, freeze- drying, heat treatment	85%	24.11 g/g	Yuan et al. (2016)
CA/CS/CMC aerogel	Simple mixing, freeze drying	>96%	43.87-80.28 g/g	This work

TABLE 1 Comparison of the as-prepared aerogel and several reported water absorbents.

(Zhang et al., 2020). Besides the excellent water adsorption properties, the S1M1A aerogel also shows great potential in separating oil-in-water emulsion and oil/water mixture. The S₁M₁A immobilized in funnel was used as the filter to evaluate separation performance. Rapeseed oil-in-water emulsion was prepared for separation experiment (Figure 9B). After the emulsion was poured into the funnel for a while, the water will flow out of the lower end of the funnel through the aerogel under the gravity. Because of the microporous structure and underwater oleophobicity (Zhang et al., 2020), the oil droplets in the upper layer cannot penetrate the aerogel saturated with water. The rapeseed oil-in-water emulsion was pale yellow and the oil droplets with uneven particle size were detected in the emulsion (Figure 9C). The filtrate after the treating is colorless and the number of oil droplets is greatly reduced in optical image (Figure 9D). It shows that S₁M₁A aerogel has good oil-inwater emulsion separation performance. The separation of oil/ water mixture was carried out using corn oil-in-water mixture as a sample (Figure 9E). After the aerogel is saturated with water, the hydrated shell in aerogel will be formed as a result of the forceful hydrogen bonds between water molecules with hydroxyl amino and carboxyl groups, which can weaken the van der Waals interaction between CA/CS/CMC composite aerogel with oil (Koh et al., 2019). In Figure 9F, the corn oil/ water mixture was cloudy and micron-sized oil droplets were detected in the mixture. Filtrate after the treatment is colorless, and there were no oil droplets in optical image (Figure 9G). The separation efficiency of water-saturated aerogels for rapeseed oil, corn oil, liquid paraffin, olive oil, motor oil and kerosene in water was over 90.7% (Figure 9H). For corn oil and liquid paraffin, the separation efficiency can reach about 96%.

4 Conclusion

In conclusion, a novel CA/CS/CMC composite aerogel with light weight, low density, high porosity, good

hydrophilic and oleophobicity, and strong water retention was synthesized through simple and green strategy. The aerogel can absorb water up to absorption capacity of 43.87-80.28 g/g. Compared with CMC and CS aerogels, the fabricated aerogel exhibits the highest water absorption capacity. As a result of strong hydrophilicity, underwater oleophobicity and water retention caused by the rough internal microstructure and the polar groups (hydroxyl, amino, and carboxyl groups), the aerogel can be used as a filter to effectively separate oil-in-water emulsions and oil/ water mixtures. The raw materials for CA/CS/CMC composite aerogel preparation are green and easy to be obtained and the preparation conditions are simple and mild, which greatly reduces the risk of secondary pollution. It is believed that the prepared aerogel displays good application prospects water treatments Li et al., 2019.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

HL: Writing—original draft, Methodology. XJ: Validation, Investigation, Visualization, Project administration. JW: Conceptualization, Supervision, Writing—review and editing. RH: Investigation, review and editing.

Funding

This research was supported by the National Natural Science Foundation of China (No. 51273154) and Graduate Innovative Fund of Wuhan Institute of Technology (No. CX2021208).

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats. 2022.1093164/full#supplementary-material

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