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Effect of β-cyclodextrin on properties of gels based on modified cellulose

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Abstract
In order to obtain a modified cellulose-based gel with good strength, adsorption property, water absorbing and water retention property, this experiment was determined the excellent process of gel preparation by controlling multiple factor condition. The cellulose matrix was prepared by dispersing nano-SiO_2 in NaOH/urea liquid system, and then adding modified cellulose (CMC) under freezing to prepare cellulose matrix. The epichlorohydrin as crosslinking agent was added to the matrix which could crosslink the cellulose to construct the cellulose chemical gel.Then the gel was tested by the mechanical test, infrared test, and swelling test. The results showed that the amount of nano-SiO_2 added, then certain amount of nano-SiO_2 was dispersed in NaOH/urea liquid system, stirred for 6 h, dissolved in cellulose under refrigeration, then added 1 mL of cross-linking agent,then added 0.5 g of β-cyclodextrin,dried at 60 °C for 12 h. This was the optimized processing parameters for the best gel performance.

Keywords: *Modified cellulose, NaOH/urea hydrogel system, β-cyclodextrin,Epichlorohydrin.*

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I. INTRODUCTION

At present, the environment and energy problems are becoming increasingly prominent, environment-friendly materials have become the goal that researchers in various fields in our country make unremitting pursuit [1]. Cellulose has many advantages such as cheap, easy to obtain, non-toxic, good renewability and environmental friendliness. It plays an important role in solving environmental and energy problems and has received wide attention. Cellulose has been considered as the main chemical source and the most abundant natural polymer in the future energy. As the most abundant natural polymer on earth, cellulose has renewable, biodegradable, biocompatible, many attractive properties, and a wide range of chemical modification capabilities. Therefore, cellulose is considered as a sustainable raw material for future energy chemical industry [2]. Therefore, exploring new "green" solvents for the dissolution of cellulose and other macromolecules and constructing "green" technology of materials are the key to exploit and utilize these natural polymer compounds. However, the solubility of cellulose affects the reactivity of cellulose to a certain extent, and the decrease of reactivity caused by low solubility becomes an obstacle to the wide application of cellulose, so modified cellulose comes into being [3].

Hydrogel is a new kind of functional polymer material with three-dimensional network structure formed by moderate physical or chemical crosslinking of water-soluble polymer with network crosslinking structure using water as dispersion medium. It is bonded by chemical bond hydrogen Van der Waals force or physical crosslinking network, formed by the entanglement of insoluble in water, but to a large number of suction height swelling and maintain fixed shape hydrophilic polymer materials [4].So far, wound dressing in personal hygiene products, such as tissue engineering. The hydrogel has been widely used as water gel hydrating mask in everyday life. The formation principle of hydrogels such as hydrogel pain-relieving paste and hydrogel fever reducing paste is that water-soluble or hydrophilic polymers can be formed through chemical or physical crosslinking [5]. The preparation of hydrogel materials by crosslinking method can be divided into three methods: chemical physical and radiation crosslinking. Chemical cross-linking refers to the formation of a network structure through the action of covalent bonds under the action of cross-linking agents. Such gel only absorbs water and expands without dissolution, which is permanent. Physical cross-linking is formed under the action of physics, but the gel disappears after heating of such gel, which is a fake gel that can be called reversible gel. Radiation crosslinking is a method of forming gels by crosslinking polymers under the action of electron beam radiation.

Cyclodextrin (CD) is a general term for a series of cyclooligosaccharides produced by amylose. It usually contains 6-12 D-glucopyranose units [7]. Among the most studied and of practical importance are molecules containing 6, 7, and 8 glucose units. Each glucose unit is combined with 1, 4-glycosidic bond to form a ring. Because glycosidic bonds connecting glucose units cannot rotate freely, cyclodextrins are not cylindrical molecules but slightly tapered rings [8]. It is structurally composed of multiple molecules linked end to end by α-1, 4-glycosidic bonds. A spiral structure in space. α, β and γ-cyclodextrin are circular oligomers composed of 6, 7 and 8 D (+) -pyryl glucose, respectively. Their molecules are wide at the top and narrow at the bottom, open at both ends, hollow tube. The inner cavity is relatively hydrophobic, while all hydroxyl groups are outside the molecule. Because a cone-shaped cyclodextrin molecule has a slightly hollow cylinder stereo annular structure, in the hollow structure, the lateral upper (open end larger) is composed of C2 and C3 para hydroxy, bottom (smaller open end) is composed of C6 primary hydroxyl, that is hydrophilic, and inside the cavity due to the shielding effect of C-H bond formed a thin water area [9]. It has neither a reducing end nor nothing more than a reducing end, that has no reducibility. It is stable in alkaline media, but can be cleaved by strong acids. It can only be hydrolyzed by α-amylase but not by β-amylase. Its tolerance to acid and general amylase is stronger than that of amylose. It crystallizes well in aqueous solution and aqueous alcohol solution.

Because the outer edge of cyclodextrin is hydrophilic and the inner cavity is hydrophobic, it can provide a hydrophobic binding site like enzyme, and act as the main body to envelope various appropriate objects, such as organic molecules, inorganic ions and gas molecules. Its hydrophobic inner cavity and hydrophilic outer characteristics make it capable of hydrophobic interaction according to van der Waals force. The matching effect between host and guest molecules forms inclusion complexes and molecular assembly systems with many organic and inorganic molecules due to the research object of interest for chemical and chemical researchers. This selective envelopment effect, commonly known as molecular recognition, results in the formation of host and guest envelopes. Cyclodextrin is an ideal host molecule similar to enzyme discoveredand it has the characteristics of enzyme model. Therefore, cyclodextrin has received great attention and been widely used in the fields of catalytic separation of food and drugs. Due to the solubility and inclusion ability of cyclodextrin in water, changing the physical and chemical properties of cyclodextrin has become one of the important purposes of chemical modification of cyclodextrin, which is also one of the objectives of this experiment [10].

In this paper, carboxymethyl cellulose was used as the main raw material to make hydrogels, and then hydrogels with different contents of β-cyclodextrin were compared and their properties were improved with chitosan. The mechanical strength test, infrared spectrum analysis and water absorption performance test of the improved gel were carried out to obtain the best ratio and technological process It provides some theoretical basis for environmental protection green aerogel.

II. MATERIALS AND METHODS

The results obtained are as discussed below

2.1 PREPARATION OF MATRIX

According to the H_2O: NaOH: Urea (200:15:8) of the corresponding raw materials, placed in 250 mL beaker, prepared into alkali/Urea solution system (NaOH/Urea=1:4), under the condition of stirring a certain amount of nano SiO_2 dispersed in the solution system. Then, the mixture was stirred vigorously for several hours at room temperature and further dispersed by ultrasound for 0.5 h. After the mixture was evenly dispersed, the mixture was put into the refrigerator (-5℃) and frozen for 6 h. After being removed from the refrigerator, the mixture was thawed at room temperature and used to dissolve cellulose. After thawing at low temperature, 3 wt% carboxymethyl cellulose was slowly added to the solution under stirring condition and left overnight.

2.2 PREPARATION OF GEL

2.2.1Screening of β-cyclodextrin dosage

A certain amount of crosslinking agent epichlohydrin (1 ml in 20 g of matrix) was accurately weighed into 20 g of matrix in a 25 ml beaker, and an appropriate amount of β-cyclodextrin was added and stirred at room temperature for 2 h. Then it was sonicated for 0.5h and placed in an oven at 60 ℃ for 12 h. After that, the hydrogel was repeatedly cleaned with distilled water. Remove bases, urea and unreacted crosslinkers from hydrogels. Mark the prepared hydrogel samples, put them in the Petri dish, wrap them with plastic wrap and mark them, and put them in a dry and cool place until use (Table 1).

Table 1: The dosageof β-cyclodextrin

No.	Matrix dosage/g	Epichlorohydrin dosage/g	Chitosan dosage/g	β-cyclodextrin dosage/g
1	20.15	1.14	0.57	1.02
2	20.25	1.17	0.54	2.01
3	20.22	1.12	0.53	3.00
4	20.16	1.13	0.55	4.02

5	20.21	1.06	0.51	5.03
6	20.24	1.09	0.55	6.01

When choose one substrate, weighing more than respectively, each 20 g in 25 mL beaker, add 1 mL of crosslinking agent of epoxy chloropropane, to join the beta cyclodextrin respectively 1 g to 6 g, then uniform slowly stir 2 h at room temperature. To avoid stirring quickly produce bubbles, the temperature was constant in incubator 60 ℃after ultrasonic drying out after 12 h. After cooling, the hydrogel was removed from the beaker, the morphology of the hydrogel was observed and the mechanical test was performed. Then, the hydrogel was repeatedly cleaned with distilled water to remove excess alkali and cross-linking agent, and the hydrogel was placed in the Petri dish, wrapped with plastic wrap and marked.

2.2.2Introduction ofβ-cyclodextrin

0.5 g chitosan was weighed, then 20 g matrix (the same matrix as the above matrix) was added, and the crosslinking agent epichlorohydrin 1 mL and β-cyclodextrin 1 g were added. The mixture was stirred slowly at a constant speed for 2 h at room temperature to avoid bubbles caused by too fast stirring. After 30 min of ultrasound, the mixture was placed in a constant temperature incubator at 60 ℃and dried for 12 h. After cooling, the hydrogel was removed from the beaker, the morphology of the hydrogel was observed and the mechanical test was performed. Then, the hydrogel was repeatedly cleaned with distilled water to remove the excess alkali and cross-linking agent. The hydrogel was wrapped with plastic wrap and marked, and the hydrogel was baked in the drying box at 60 ℃until it became dry without moisture, and then the relevant swelling and FTIR test were performed.

2.2.3Preparation of Aerogel

Freeze-drying can be divided into three stages: freeze-sublimation-redrying. The prepared hydrogel was frozen in the refrigerator at -80 ℃for 30 h or in liquid nitrogen for 5 minutes to make the hydrogel completely frozen. Then, the hydrogel was put into the freeze dryer which had been reduced to -40 ℃. During the freeze-drying period, the temperature was about -50 ℃and the vacuum degree was about 0.1mbar. Place in a sealed bag and mark for testing.

2.3 MECHANICAL PROPERTIES AND MORPHOLOGICAL CHARACTERIZATION

Put 50 g weight on the top of the prepared hydrogel sample, observe its deformation state and resilience, and judge its strength and toughness. The advantages and disadvantages of hydrogels were analyzed and judged by macroscopic observation.

2.4 FTIR ANALYSIS

A certain amount of freeze-dried hydrogel samples and KBr powder were mixed and ground evenly in an agate mortar and then pressed into tablets. The infrared spectrum of the samples was obtained by FTIR. The scanning wavelength range is 400~4000 cm^{-1}.

2.4 SWELLING PERFORMANCE

The swelling performance of hydrogels was tested by grametry. The freeze-dried aerogel samples were cut into 1.0cm x 1.0cm size samples, and the weight of each cut aerogel sample (W_d) was weighed, and then soaked in sufficient amount of deionized water at room temperature every 10min. The soaked sample was taken out with tweezers, and the moisture on the surface of the sample was absorbed with filter paper. After that, it was weighed with electronic balance (W_t). Six groups of data were tested for each sample, and the swelling rate of aerogel was calculated by recording and using the following formula (1), and the line chart of swelling rate was drawn.

$$SR = (W_t — W_d) / W_d \quad (1)$$

III. RESULT AND DISCUSSION

3.1 EFFECT OF β-CYCLODEXTRIN ON MECHANICAL AND MORPHOLOGICAL CHARACTERIZATION OF GELS

The dosage of β-cyclodextrin affects the morphology and strength of hydrogel. As shown in Figure 1, it can be seen from the figure that hydrogels prepared by adding 2 g to 6 g β-cyclodextrin are not in good condition after drying for 12 h. Most hydrogels are flow-like and do not take shape after cooling. With beta cyclodextrin 6 g of water gel, stirring after 2 h, mixture distribution in the material such as grain samples.The main reason lies in the beta cyclodextrin scattered among them, 12 h after drying, the extra beta cyclodextrin still exists, the overall appeared saturated state, distribution on the surface of hydrogels form a layer of a hard shell, the lower is soft, the overall forming, The morphology, strength and network structure of hydrogels are affected, and then the properties of hydrogels are affected. The hydrogels with 2 g to 6 g of β-cyclodextrin had poor mechanical properties, and the strength was not as strong as the hydrogels with 1 g of β-cyclodextrin. As shown in Figure 1-A, the hydrogel made by adding 1 g β-cyclodextrin can be seen from macroscopic morphology observation and qualitative mechanical test that the hydrogel prepared by adding 1 g β-cyclodextrin is stable and formed after

drying for 12 h, with certain strength, elasticity and transparency, and the effect is better after adding 0.5 g chitosan.

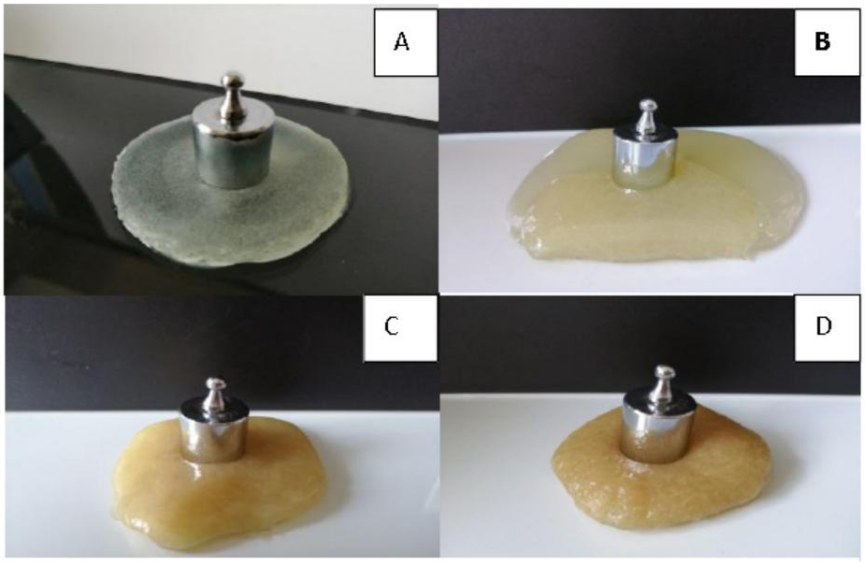

Figure 1: Mechanical Propertiesof Hydrogels with Different β-cyclodextrin Dosage (A: 1g; B: 2 g; C: 4 g; D: 6 g)

Therefore, the content of β-cyclodextrin plays an important role in the preparation of hydrogels, which directly affects the cross-linking density of the hydrogel network. With the increase of the amount of β-cyclodextrin, the hydrogel formed is an unstable and soluble gel network with too strong fluidity. When the content of β-cyclodextrin exceeds 6 g. The excess β-cyclodextrin will be distributed on the surface and inside of the hydrogel and affect the network structure of the hydrogel, the morphology and strength of the hydrogel. Therefore, it isnot betterthat the more β-cyclodextrin. Judging from the observation of gel morphology characterization, the shape, strength, toughness and transparency of the gel with 1 g β-cyclodextrin are the best. In conclusion, as the water gel has good strength and toughness is prepared, such as β-cyclodextrin dosage was 1 g.

3.2 EFFECT OF CHITOSAN ON MECHANICAL AND MORPHOLOGICAL CHARACTERIZATION OF GELS

The shape of hydrogel made by adding chitosan is stable after removal, and there is no deformation after placing the weight, and the original shape is quickly restored after removing the weight. The hydrogel made by adding only β-cyclodextrin was stable when it was dried for 12 h, and slightly fell into the inside of the gel when the weight was placed. Therefore, the hydrogel made by adding chitosan is more stable, strong and tough, and saves energy and time. We can clearly see the difference after freeze drying and swelling tests.As shown in Figure 2, the cross-linking effect was increased by adding chitosan. Hydrogels with a high degree of chitosan association usually have a high degree of deformation ability, and the chemical cross-linking network structure of hydrogels with chitosan addition tends to be perfect. To make the hydrogel more perfect.

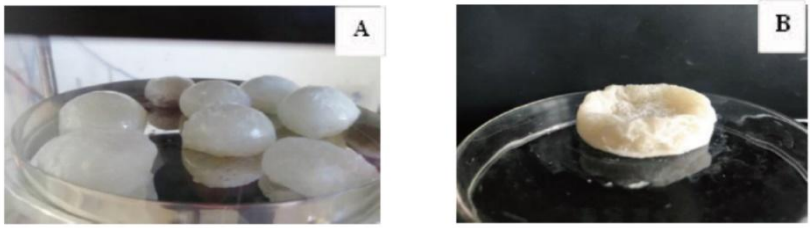

Figure 2: Hydrogel Freeze-driedwith β-cyclodextrin and Chitosan (A: in process; B: After the process)

3.3 SWELLING PERFORMANCE ANALYSIS

As you can see from Figure 3, only to join epichlorohydrin preparation, epoxy chloropropane and β-cyclodextrin, join epoxy chloropropane, β-cyclodextrin and three of the preparation of chitosan gel obvious difference after soaked for a period of time, gel containing different content of epoxy chloropropane after soaking also have difference. In particular, the hydrogel added with epichchlorohydrin 1g, β-cyclodextrin 1g and

chitosan 0.5g was stable and in good shape during the whole soaking process, without any fragmentation phenomenon, that is, the internal network structure of the hydrogel changed little or even remained unchanged, which would not affect the performance of the hydrogel.

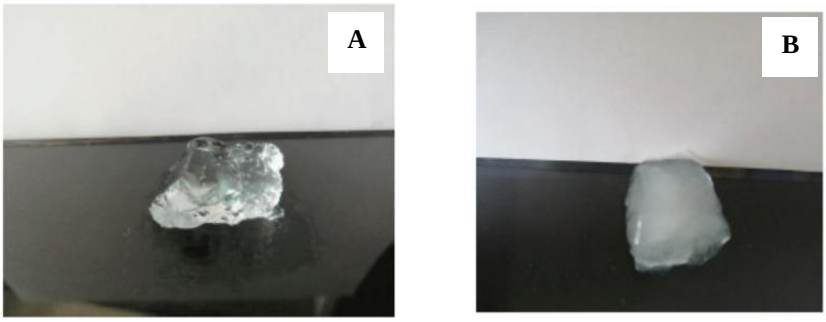

Figure 3: Swelling Test (A: containing epichlorohydrin; B: containing chitosan, epichlorohydrin and β-cyclodextrin)

The hydrogel containing epichlorohydrin without introducing other substances has no original shape and structure after soaking overnight, and the structure does not change in application is the basis of property maintenance. So, the stability of the structure is crucial to the performance of a substance. In figure 3, we know that only with 1 g of epoxy chloropropane hydrogel swelling or even broken separation with immersion time lengthen, epoxy chloropropane and add 1 g β-cyclodextrin hydrogel performance is not good. When 1 gepoxy chloropropane and 1 g β-cyclodextrin and 0.5 g of chitosan were added, the hydrogel swelling effect was similar to 2 g epoxy chloropropane. However, because epichlorohydrin has moderate toxicity and potential carcinogenic risk, it should not be used more.The results showed that the test is successful and has practical application value.

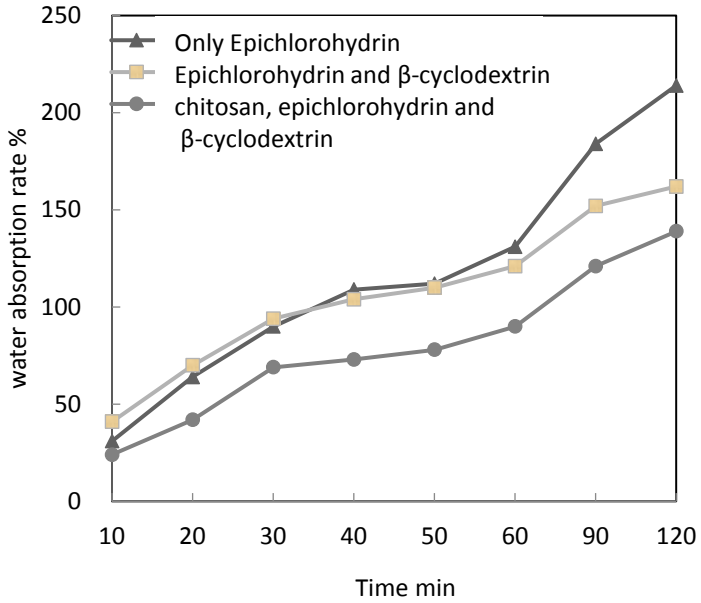

Figure 4: Swelling Test

It can be seen from Figure 4 that in the first half of the period, the water absorption rate of hydrogels prepared by adding epichlorohydrin and β-cyclodextrin is almost the same as that of hydrogels only adding epichlorohydrin in the early stage, and the hydrogels containing β-cyclodextrin are slightly better.But the overall curve is almost the same. With the extension of the 60 min, there was a significant difference in the water absorption rate of the hydrogel containing only epichlorohydrin. The water absorption rate of hydrogels prepared by adding epichlorohydrin, β-cyclodextrin and chitosan has been relatively stable and continued to increase. In the later stage, the water absorption rate of hydrogels prepared by adding epichlorohydrin and β-cyclodextrin will surpass that of hydrogels prepared by adding epichlorohydrin and β-cyclodextrin with good performance. In conclusion, the hydrogels prepared by adding β-cyclodextrin and chitosan have the best

mechanical properties, swelling properties and stability, indicating that it is necessary for them to exist at the same time.

According to the results, the sample water absorption expansion rate is slow but stable upward trend, then bibulous rate rises late and there are beyond the trend. The stable traits were not broken, reached the maximum in modified cellulose hydrogel introduced in beta cyclodextrins and does not destroy modified cellulose hydrogel performance goal. The experiment has come to a successful conclusion.

3.4 FTIR ANALYSIS

Because chitosan itself can be degraded, and be degraded by a variety of methods, and the cost is relatively low. Itisno toxic, no side effects and no environmental pollution. Chitosan with biocompatibility and biodegradability can be developed through the action of crosslinking agents.

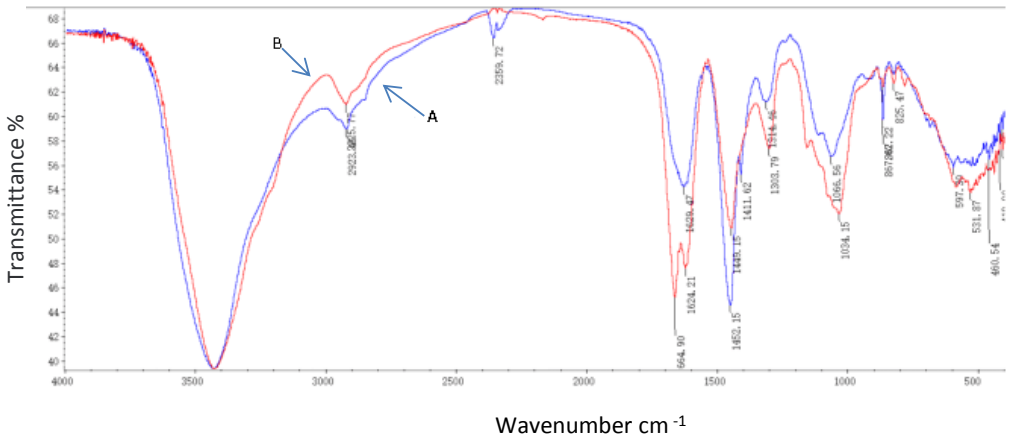

Figure 5: FTIR of aerogels (A: containing epichlorohydrin; B: containing chitosan, epichlorohydrin and β-cyclodextrin)

When A variety of polymers are compatible, there will be obvious interaction between molecules. It can be seen from infrared spectrum Figure 5 that the absorption peaks of gel A at 3400 cm^{-1} and 1065 cm^{-1} are broadened, which is caused by the introduction of β-Cd with A large number of -OH groups. The stretching vibration peak of N-O-C at 1034 cm^{-1} is enhanced. This indicates that the hydroxyl group structure in chitosan is cross-linked with the carboxyl group in cellulose, which also enhances the internal network structure of the gel, thus improving the mechanical properties and swelling properties. Previous studies have shown that the toxicity of hydrogels is very low or even negligible in large systems [8]. Similarly verifiable, good biocompatibility is a good advantage of water gel itself, in terms of sustained release and tissue engineering field has a broad prospect of application technology, CS composite hydrogel have suitable for cartilage repair network structure and the equilibrium moisture content of alternative materials, CS enhancement is given to the interaction of water and gel. The biocompatibility and degradation ability of the gel are optimized, which can be used as a model system for theoretical research and practical operation in the future.

IV. CONCLUSION

The best process of this experiment is: stirring the matrix for 6 h and freezing, dispersing 1 times the amount of nano-SiO_2 (0.20 g) in the alkali/urea solution system, 7g carboxymethyl cellulose, introducing 0.5g chitosan, 1mLcrosslinking agent epichlorohydrin, 1gβ-cyclodextrin, and drying at 60 ℃ for 12 h.

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