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Structural characterization and properties of sustained - release microcapsules containing polylactic acid starch compound sustained release drugs

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Abstract. To research structure and analyze property of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs, this paper prepares material/starch sustained release carbon and makes experimental analysis to it. Firstly, set interval denitrification test with optimizing polylactic acid/starch mixture ratio, make continuous dynamic test for denitrification packing column, and give schematic model of test device of denitrification packing column. Secondly, make experiment on FTIR characteristic of microcapsules containing polylactic acid starch compound sustained release drugs, give TG analysis of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs and scanning electron microscope result to MD, MD+WPC, CS+MD+WPC and polylactic acid starch and analyze fine structure of sustained-release microcapsules. Experimental result can present sustained-release microcapsules property of polylactic acid starch compound sustained release drugs sufficiently, so it is applicable to practical application guidance.

Key words. Polylactic acid starch, Sustained release drugs, Microcapsules, Structural analysis.

1. Introduction

As mature industrialization technology, microencapsulation technology is widely applied to industry field, such as food, medicine and feed etc. Microencapsulation wall material is the key of efficient microencapsulation. Compound wall material

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conforming to film-forming property and emulsifying property requirements with low cost, wide source and abundant nutrition becomes the first choice.

Microcapsule includes 2 basic components, and matter wrapped in the microcapsule is called as core material while external "shell" is called as wall material. In preparation process of microcapsule, wall material can separate core material from external environment and releases core material under proper conditions. Specific action of wall material to core material makes microcapsule technology widely applied to many fields, such as food, chemical industry, medicine and biotechnology etc. and has obvious advantages: improve physical property (such as color, appearance and solubleness) of core material; control release of core material; make core material free from effect of unfavorable factors at the external environment (such as light, oxygen, temperature and humidity) and improve matter reliability; separate insoluble matter; conceal bad flavor and color and luster; reduce additive amount and toxic and side effect etc. of food additives. Microencapsulation method is mainly selected on the basis of application occasion, industrial production scale and production cost etc. of microcapsule. Common microencapsulation technology mainly includes: spray drying, extrusion method, coagulation method, air suspension method and molecular inclusion etc. Spray drying is most widely used in food field because of mature process and low cost. With continuous appearance of new material, microencapsulation methods have turned to include 200 types, but a set of systematic classification method has not been established yet. Some scholars divide these methods into 3 types according to microcapsule nature, capsule wall formation mechanism and encystation condition, i.e. chemical method, physical-chemical method and physical method.

In recent years, scholars have researched solid-phase denitrification process, and characteristic of the process is mainly that organic carbon matter with loose structure is adopted as carbon source and biofilm carrier, and operation of the process is simple with steady operation and wide range of application. Natural polymer material can realize steady supply after transformation, which guarantees exuberant metabolism of microorganism, improves removal efficiency of pollutant, and has good biocompatibility and low cost etc. Starch is one of important biological nutrient ingredients, it can generate maltose and glucose etc. through hydrolysis and source of raw material is wide. Degradation product of polylactic acid is lactic acid being matter required in normal metabolism of human body and being characterized by the fact that it is free from any toxicity and side effects. Therefore, this research mixes polylactic acid and starch together to prepare sustained release carbon having carbon source and biofilm carrier effect, and investigates removal variation of sustained release carbon with different quality P:S to nitrate nitrogen pollutant etc. in denitrification interval test to select polylactic acid/starch mixture ratio with the best denitrification effect and apply it to continuous dynamic test to improve denitrification efficiency maximally and lower process operation cost, thus providing data basis for development and application of new sustained release carbon source.

2. Material and method

2.1. Preparation of polylactic acid/starch sustained release carbon

Take polylactic acid particle (purchased from Shenzhen Guanghua Weiye Industry Co., Ltd.) of which molecular weight is 80 thousand and starch commercially available as raw material, add polylactic acid particle and starch to high-speed pulverizer (HY-04B, Beijing Huanyatianyuan Mechanical Technology Co., Ltd.) on the basis of certain mass ratio and smash and mix them evenly, and add them to injection molding machine (JP6C-9, Beijing Yingte Plastic Machinery Central Plant) of which temperature has risen to 100∼180° slowly with constant speed to squeeze out cylinder with 0.3cm diameter roughly, and cut off the cylinder into short cylinder with 2cm length roughly after cooling under room temperature. Sustained release carbon material is as shown in Fig.1.

Fig. 1. Polylactic acid/starch sustained release carbon material

2.2. Interval denitrification test with optimizing polylactic acid/starch mixture ratio

Add 10g polylactic acid/starch sustained release carbon of which mixture ratio respectively is 8:2, 7:3, 6:4 and 5:5 and 150mL distilled water to 4 250mL conical flasks, and add 0.028mL methanol (liquid carbon source) to another 250mL conical flask as control group. Add KNO3 and NaH2PO4 to make concentration of nitrate nitrogen and total phosphorus respectively be 50mg·L-1 and 10mg·L-1. Add activated sludge after denitrification domestication and control concentration of sludge within 800mg·L-1. Adjust pH to 7.5. Seal the flask and place conical flask into constant-temperature oscillator with 70r·min-1 revolving speed and temperature controlled within 25°±1°. Change and add 150mL waste water prepared manually with nitrate every day for 16d continuous operation, and sample per 24h to analyze concentration of nitrate nitrogen, nitrous nitrogen and COD.

2.3. Continuous dynamic test for denitrification packing column

Test is made within up-flow packing column. The packing column is cylinder made of organic glass with 100mm inner diameter and 450mm height and 1L effective packing volume. 300g sustained release carbon with the best polylactic acid/starch mixture ratio is selected through packing. Place sustained release carbon into denitrification sludge after domestication for immersion, mix it evenly, and place sustained release carbon into packing column for biofilm culturing after inoculation. Good treatment effect of water feed (inflowing nitrate nitrogen concentration is 50mg·L-1 and temperature is 25°±1°) reactor can be realized after 1d, which shows that biofilm culturing speed of the sustained release carbon is quick. Whereafter, investigate denitrification effect of reactor in continuous and steady water feed and sample regularly to analyze inflowing and outflowing nitrate nitrogen, nitrous nitrogen, ammonia nitrogen, pH and COD. Fig.2 is schematic diagram of device of continuous dynamic test.

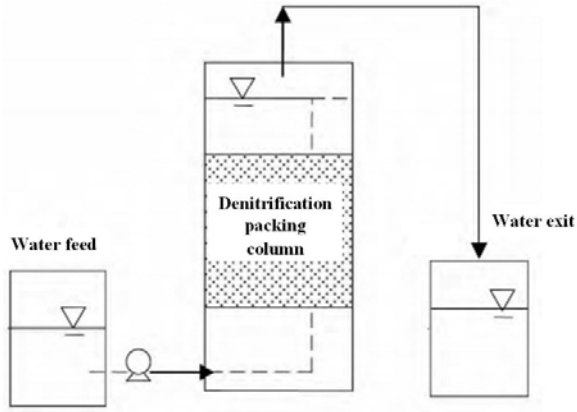

Fig. 2. Schematic diagram of test device of denitrification packing column

3. Result analysis

3.1. FTIR characterization result of microcapsule containing polylactic acid starch compound sustained release drugs

See Fig.3 for FTIR spectrogram of carbofuran and blank microcapsule and sustained-release microcapsules containing polylactic acid starch compound sustained release drugs. Seen from Fig.3, overlaying spectrogram of spectrogram c, spectrogram a and spectrogram b is similar, which shows that sustained-release microcapsules containing polylactic acid starch compound sustained release drugs have wrapped carbofuran. In spectrogram b, stretching vibration strong characteristic absorption peak of -N-C-S perssad does not appear at adjacent area of 2000cm-1, but stretching

vibration absorption peak of C-S key appears at 1200cm-1 and stretching vibration absorption peak of C-O key appears at 1 710 cm-1, which shows that microcapsule composited includes sulfur vein perssad.

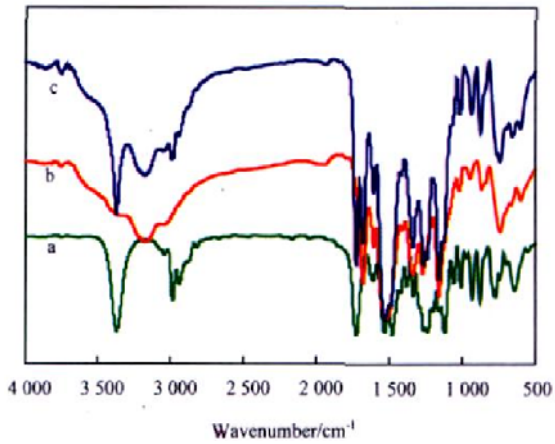

Fig. 3. FTIR spectrum of carbofuran and blank microcapsule and sustained-release microcapsules containing polylactic acid starch compound sustained release drugs

3.2. TG analysis of microcapsules containing polylactic acid starch compound sustained release drugs

Thermogravimetric analysis is a kind of technology to measure relationship between mass and temperature of matter. It records mass variation of matter analyzed in temperature-rise period, so heat stability and degradation process of matter can be reflected. Thermogravimetric curve (TG curve) represents weight loss cumulant of matter in temperature-rise period and the curve shape generally is curve with transition and incline sections. Instantaneous weight loss rate can be calculated when a differentiation processing is made to TG curve, which is DTG curve and it represents severity in the case of weight loss caused by resolving and combustion. Peak temperature of DTG curve represents corresponding temperature of the maximum weight loss rate, peak height of DTG represents size of the maximum weight loss rate, and therefore combination of TG-DTG can analyze product heat stability better. This paper determines TG-DTG curve of butter and blank microcapsule and sustained-release microcapsules containing polylactic acid starch compound sustained release drugs, analyzes pyrogenic decomposition process and heat effect law of the matter in detail and researches nature of microcapsule product, and compares with TG-DTG curve of butter and blank microcapsule simultaneously to analyze heat stability effect of microencapsulation on sustained-release microcapsules containing polylactic acid starch compound sustained release drugs.

Seen from Fig.4, weight loss of sustained-release microcapsule sample of butter sustained release drugs can be divided into 2 stages with temperature variation.

Temperature range at the first stage is 80.00-150.00 ° and sample weight loss is 12.5% at the stage because of overflow of moisture and a little of micromolecule matter. DTG weight loss rate peak corresponds to TG weight loss peak obviously and mass loss at the stage is relatively great, which shows that product moisture content is relatively great. Temperature range at the second stage is 200∼450 °. A main peak of DTG appears, TG curve declines obviously, and sample weight loss is 87.1% because of resolving of butter.

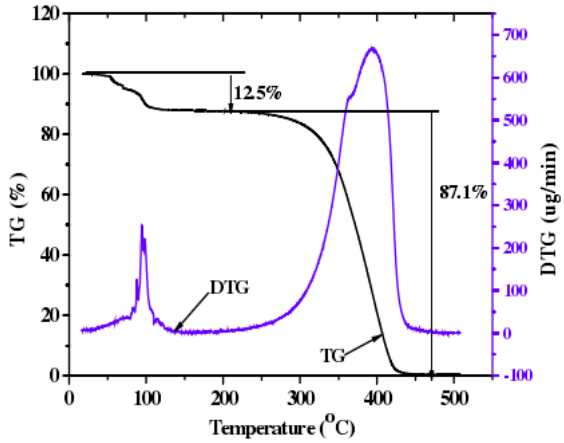

Fig. 4. Spectrogram of butter sustained-release microcapsule

Fig.5 is TG-DTG spectrogram of blank microcapsule. Sample weight loss in the figure is mainly divided into 3 stages. 1) At water evaporation stage, weight loss is 4.5, which shows that moisture content of microcapsule sample is low, and it is the same with moisture content result determined formerly. 2) Within 140250 ° temperature range, sample weight loss is 22.5%, a main peak of DTG appears at 210°, and TG curve declines. Because phase-transition temperature of maltodextrin is the minimum in all wall material components, weight loss is sourced form resolving of partial maltodextrin. 3) Within 250390 ° temperature range, sample is resolved again. A maximum weight loss rate value of DTG curve appears at 310 oC, TG curve declines obviously, and sample weight loss is 37.3%, and it may be caused by resolving of wall material maltodextrin and protein component through analysis. (4) With further rise of temperature, sample is resolved continuously, but weight loss rate lowers gradually until it is relatively steady.

Fig.6 is TG-DTG spectrogram of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs. Sample weight loss is mainly divided into 3 stages. Weight loss is 3.2% at the first stage, which shows that moisture content of microcapsule sample is low, and it is the same with moisture content result determined formerly. Within 200∼350° temperature range, 2 DTG main peaks appear, and weight loss respectively is 19.5% and 18.1% and sourced from resolving of wall material. After temperature is greater than 350°, sample is resolved again. When temperature is 560°, sample weight loss is 29.8% and mainly caused by resolving starting of sustained-release microcapsules containing polylactic

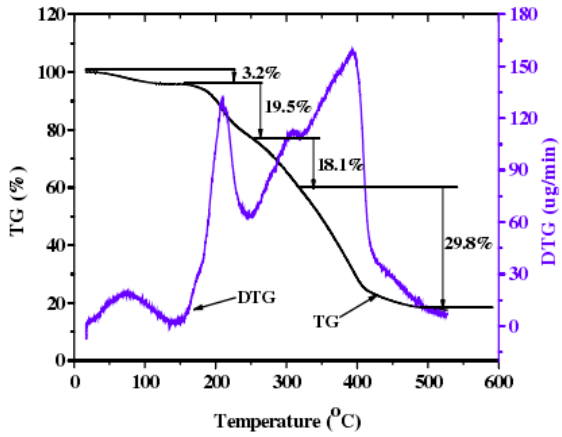

Fig. 5. TG-DTG spectrogram of blank microcapsule

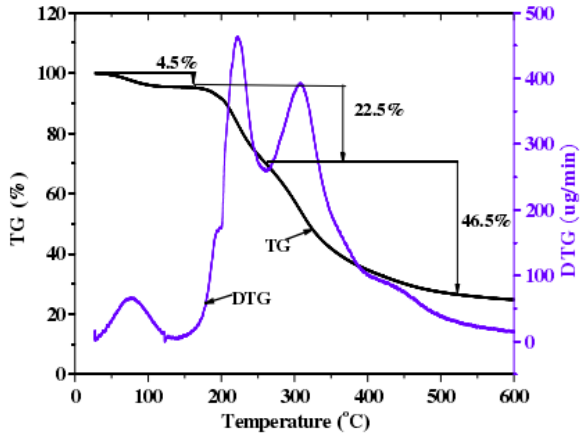

Fig. 6. TG-DTG spectrogram of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs

acid starch compound sustained release drugs at the internal.

Through comparison of Fig.4, Fig.5 and Fig.6, it can be found that TG-DTG curve of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs is obviously different from another 2 TG-DTG curves. Through microencapsulation, decomposition temperature of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs moves backward, lengthening from original 200° to 350° and the reason is that sustained-release microcapsules containing polylactic acid starch compound sustained release drugs are wrapped in internal of wall material through microencapsulation and new form is formed, which simultaneously shows that embedding effect is comparatively good and product heat stability is good. It is simultaneously found that after the third weight loss peak of butter and blank microcapsule appears, the fourth weight loss

peak appears later and wall material weight loss rate is 37.6% that differs from theoretical wall material weight in relatively great degree, which shows that butter is not wrapped in internal of wall material totally, but is distributed among wall material in the form of inlay almost.

3.3. Scanning result analysis

Selection of proper wall material is a quite important step for microcapsule preparation. Protective effect and sustained or controlled release effect of microcapsule to core material depend on wall material component selected. Wall material selected can give play to barrier function on the one hand, protecting core materials from being affected by oxygen, water and light, avoiding contact of core materials with other component effectively, and controlling diffusion of core materials effectively in a certain degree. On the other hand, wall material used for microencapsulated grease must have relatively stability, strong water solubility, easy drying (superfine and compact network will be formed in drying process) and strong emulsibility (separation of lipid from emulsion is forbidden in drying process). Commonly-used wall material includes protein WPC (soyabean protein) and hydrocolloid (modified starch and acacia gum). Hydrolyzed starch MD (glucose, lactose and corn syrup) is generally added as auxiliary wall material CS to improve drying property. But it is quite difficult to realize great embedding effect with single wall material, and great effect can only be realized through compound of numerous wall materials.

CS has good emulsifying and film formation capacity. It can be used as oxygen barrier because of low cost, good dispersibility and solubleness and easy combination with fat, commonly used as microcapsule wall material embedding food ingredient, such as milk powder and fruit and vegetable drinks etc. WPC has specific milk flavor, and comparatively good emulsibility and solubleness. But additive amount will be comparatively great and cost will be relatively high if good embedding effect needs to be realized with a kind of single matter as wall material, and for example, if single MD is taken as wall material, the additive amount has to be 50% to be used in bayberry juice embedding. This part mainly investigates influence of compound effect of MD, CS and WPC on the form by taking them as wall materials.

Seen from Fig.7, product taking MD as wall material is not distributed in uniform way, particle size difference among particles is comparatively large, while particle size of product containing protein is relatively uniform, and polylactic acid starch granule is distributed in the most uniform way. According to literature, sample taking single MD as wall material will be dried with matter wrapped in the form of physical mixture in drying process because MD does not have surface activity. For sample taking MD and protein as compound wall materials, protective film can be formed between gas/water interfaces in drying process because protein has good emulsibility to wrap matter wrapped. Within view range, capsule walls of all samples are relatively complete and wall breaking is not found, but it is simultaneously found that irregularity of relatively little particle is comparatively high and a great deal of sinking appears at the surface. Just as reported by Rosenberg et al, surface structure of microcapsule is closely concerned with drying temperature, and comparatively

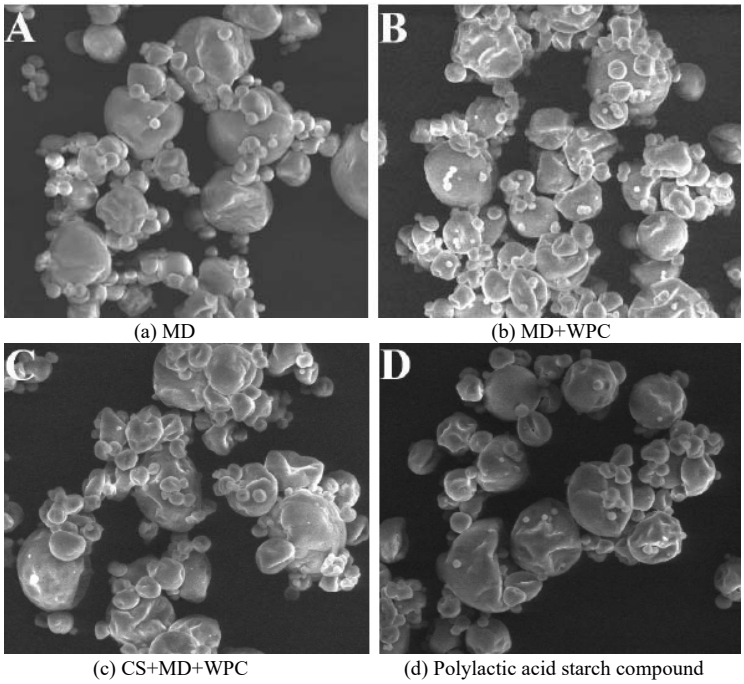

Fig. 7. Scanning electron microscope figure of sustained-release microcapsules consisting of different wall materials

high temperature will cause fast setting and sinking of wall material easily, so little granule with smooth surface will not be formed easily, which shows that solidification of wall material is faster than expansion and round formation of microcapsule.

4. Conclusion

This paper researches structure and analyzes property of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs, sets interval denitrification test with optimizing polylactic acid/starch mixture ratio, and makes continuous dynamic test for denitrification packing column, makes experiment on FTIR characteristic of microcapsules containing polylactic acid starch compound sustained release drugs and gives TG analysis of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs and scanning electron microscope result to MD, MD+WPC, CS+MD+WPC and polylactic acid starch. Experimental result can present sustained-release microcapsules property of polylactic acid starch compound sustained release drugs sufficiently. Research direction in next step: (1) make deep optimization to experimental structure; (2) optimize structure of sustained-release microcapsules containing polylactic acid starch compound sustained release drugs; (3) research and develop actual application product.

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