Preparation of β-Cyclodextrin modified Polystyrene Nanofiber and Its Application in the Extraction of Rhodamine B

Ren-Shan ZHAO1,a, Xue-Jun KANG1,b,* and Jian-Jun DENG2,c

1Key Laboratory of Child Development and Learning Science (Ministry of Education), Research Center for Learning Science, Southeast University, Nanjing, China, 210096
2Suzhou Dongqi Biological Technology Co., LTD, Suzhou, 215123, China
a zrs0202@163.com, b xjkang64@163.com, c djj_real@126.com
*Corresponding author

Keywords: β-Cyclodextrin, Rhodamine B, Packed-fiber solid-phase extraction.

Abstract. An unique pretreatment and detection of rhodamine B in chilli samples was described. The pretreatment method was based on β-Cyclodextrin modified polystyrene (PS) nanofiber. The modified nanofiber obtained was studied by scanning electron microscopy and fourier transform infrared spectroscopy, respectively. The modified PS nanofiber extraction efficiency was higher than unmodified PS nanofiber.

Introduction

Rhodamine B (RB) was usually used as a colorant in textiles and was a well-known fluorescent tracer [1]. Although it is poisonous for human beings and animals, some illegal traders still use it as a food additive [2]. However, direct determination of RB is very difficult because of the low content in samples and the matrix effects [3, 4]. Thus, it is necessary to develop a pretreatment method for the sample containing RB.

Solid-phase extraction (SPE) is a frequently-used pretreatment method because of its simplicity and rapid phase separation. Some novel functional materials such as activated carbon [5], zeolites [6] and polymeric adsorbents [7] have been used for SPE. Recently a novel solid-phase extraction (SPE) method based on the use of electrospun polymer nanofibers as the absorbent for the preconcentration of the target substances was developed [8]. Although electrospun nanofiber technique was reported in the early 1970s and various applications in many domains have been reported after that [9], the electrospun nanofiber has been used in pretreatment for extraction target substances from bio-samples until recent years. A typical example of this novel SPE method called packed-fiber solid phase extraction (PFSPE) [10]. Compared with conventional extraction materials, the electrospun nanofiber was convenient to be modified [11]. Among the functional materials, β-Cyclodextrin (β-CD) has attracted particular attention, due to its unique availability, physico-chemical characteristics and low cost [12]. The central cavity of cyclodextrins, which is lined with methylene hydrogens and glycosidic oxygen bridges, is relatively hydrophobic compared to water [13].

In this work, β-CD modified polystyrene nanofiber was obtained. Scanning electron microscopy (SEM) was used to study the morphology and diameter range of nanofiber. Fourier transform infrared spectroscopy (FTIR) was used to make sure that the polystyrene nanofiber was modified by β-CD. The PFSPE based on β-CD modified polystyrene nanofiber was investigated for the extraction of RB in real samples.

Experimental

Chemicals and Materials

All chemicals used in this work were of analytical reagent grade and were utilized without further purification, β-Cyclodextrin (β-CD), N, N-dimethylformamide (DMF), tetrahydrofuran (THF), ethanol,
methanol and acetonitrile were purchased from Yuwang Chemical Reagent Company, China. Standard rhodamine B (RB) and polystyrene (PS, 99%, Mw=185,000) were provided by Sinopharm Chemical Reagent Company, China.

**Preparation of Nanofiber**

The properties of modified nanofiber were significantly influenced by the ratio of modified substance, thus, 5%, 10% and 15% β-CD (m:m) and 1g PS were added into a mixed solvent composed of N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) (4:6, v/v), then the mixture was stirred slowly at room temperature for 4 h. Moreover, the voltage of electrostatic spinning and working distance were other key factors that could change the morphology of nanofiber. Thus, 8kv, 10kv, 13kv and 15kv of electrostatic spinning and 18, 20 and 22 cm working distance were selected to investigate the best conditions.

**Characterization**

A scanning electron microscopy (SEM) image was recorded with a field emission ZEISS SEM. Fourier transform infrared spectroscopy (FTIR) of the nanofiber was recorded on a BRUK ERVECTOR 22 spectrometer.

**Preparation of Packed Nanofiber Solid Extraction Columns**

The solid-phase extraction column used in this study was prepared by filling 6 mg nanofibers in the thin bottom of the column (see Fig. 1). Before extraction, the PFSPE column was activated by 100 µL methanol and 200 µL water, respectively. The solvents was loaded and eluted through the column by the pressure of air from a gas tight plastic syringe.

![Figure 1. Schematic diagram for PFSPE column.](image)

**Extraction of RB in Samples**

Standard stock solution of RB was prepared at 1mg/mL in methanol and stored at 4°C in the dark. The working solutions were prepared as appropriate dilution of the stock solutions.

Chili sample was purchased from a market of Nanjing, China, and all of which without detectable RB were used as blank samples. The sample was prepared as following: weighting 1g of the crushed chili sample; adding 10 mL ultrapure water, and sonディング the mixture for 10 min and centrifuging it at 4000 rpm for 10 min, then separating the supernatant.

The samples used for the extraction experiment were RB spiked water and supernatant of Chili sample. 2 mL of the spiked sample was loaded and pushed through the sorbent by the pressure of air forced by a gas tight plastic syringe. The RB retained on the PFSPE was eluted with the 100μL of methanol and the eluate (10µL) was injected into the HPLC for determination.
**Instrumental Analysis**

The column used was Inertsil C18 (250mm×4.6mm, 5 µm). The wavelength was 550. The mobile phase was composed of an aqueous mobile phase (3 g/L phosphate buffer) and methanol (30:70, v/v) and was adjusted to pH 7.0 with phosphoric acid. The flow rate was 1.0 mL/min. The injection volume was 10 µL.

**Results and Discussion**

**Characterization of the Modified Nanofiber**

In the mixtures of β-CD, PS, and the mixed solvent, only 5% β-CD and PS mixed compounds could be fully dissolved. Thus, 5%β-CD -PS solution was selected. The diameter range of nanofiber in different voltage of electrostatic spinning was showed in Fig. 2. Apparently in Fig. 2, when the voltage is gradually increases, the diameters of the nanofibers increase gradually. Furthermore, with the voltage was higher than 13 kv, the beads on the nanofiber was disappeared. Thus, the best voltage of electrostatic spinning should be higher than 13 kv. The diameter range of nanofiber in different voltage of electrostatic spinning was showed in Fig. 3. The diameters of the nanofibers diminish gradually when the working distance increases. Thus, the best working distance was 22 cm.

![Figure 2](image2.png)

**Figure 2.** The diameter range of nanofiber in different voltage.

![Figure 3](image3.png)

**Figure 3.** The diameter range of nanofiber in different working distance.

The FTIR images of PS and β-CD modified PS were showed in Fig. 4. Comparing the two images, PS -β-CD holds two characteristic absorption peaks at 3372 and 1679 cm⁻¹, due to stretching and the
bending, respectively, of the O-H groups of β-CD, as well as a peak at 1028 cm\(^{-1}\) due to the C-O-C asymmetric stretching, which means β-CD modified PS has been successfully obtained.

![FTIR image of nanofibers](image)

**Figure 4. The FTIR image of nanofibers.**

**Extraction of RB in samples**

The extraction efficiency of RB onto PS and PS-β-CD nanofibers were showed in Fig. 5. All the extraction efficiencies of RB on the β-CD modified PS fibers were higher than that on PS fibers, which means β-CD modified PS was more suitable for the extraction of RB.

![Extraction efficiency of RB](image)

**Figure 5. The extraction efficiency of RB onto PS and PS-β-CD nanofibers.**

**Acknowledgement**

This work was supported by the National Science Foundation of China (No. 81172720, 81673230), the National Instrumental Research Program (2014YQ06077303), and the Science and Technology Program of Jiangsu Province (No. BE2016741).

**References**


