Journal of Colloid and Interface Science 527 (2018) 124–131

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

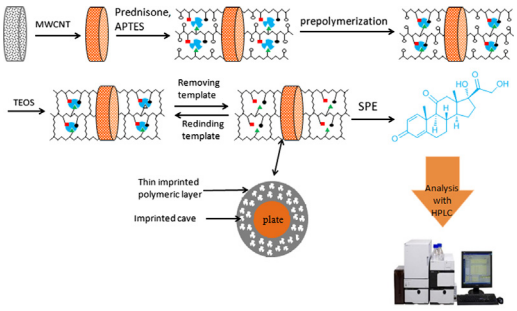
Regular Article

Preparation and application of a molecular capture for safety detection of cosmetics based on surface imprinting and multi-walled carbon nanotubes

Fang Wang [a], Xiaoyan Li [a,*], Junjie Li [b], Chen Zhu [a], Min Liu [a], Zongyuan Wu [a], Li Liu [a], Xuecai Tan [a], Fuhou Lei [a]

[a] School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Key Laboratory of Guangxi Colleges and Universities for Food Safety and Pharmaceutical Analytical Chemistry, Guangxi Key Laboratory of Chemistry and Engineering of Forest Products, Guangxi Colleges and Universities Key Laboratory of Utilization of Microbial and Botanical Resources, Nanning, Guangxi 530008, China
[b] School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 February 2018
Revised 11 May 2018
Accepted 13 May 2018
Available online 14 May 2018

Keywords:
Molecular capture
Solid phase extraction
Multi-walled carbon nanotubes
Cosmetic samples
Prednisone
HPLC

ABSTRACT

A novel composite material for prednisone molecular capture (PS-MC) was prepared by surface imprinting technique in combination with a polyethylene filter plate coated with multi-walled carbon nanotubes for the first time. PS-MC was achieved by using prednisone as the template molecule, 3-aminopropyltriethoxysilane as the monomer, and tetraethoxysilane as the cross-linker. The structure, morphology, and thermal stability of the prepared PS-MC were studied by fourier-transform infrared spectrometry, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, and thermogravimetric analysis. PS-MC was assessed by re-binding experiments such as adsorption kinetics, adsorption isotherms, molecular identification, and applied to the separation and enrichment of prednisone in cosmetics. The results indicated that PS-MC has rapid binding kinetic, high adsorption capacity, and favorable reusability. The imprinted materials were coupled with HPLC to selectively separation, purification, and detection of prednisone from spiked cosmetic samples. The recoveries of spiked cosmetic samples were in the range of 83.0–106.0%, with relative standard deviations of less than 2.10%, and the limit of detection of 5 ng/mL (S/N = 3).

1. Introduction

Prednisone, an intermediate-acting glucocorticoid, is commonly used in the treatment of hematologic and dermatologic diseases, nephritic syndrome, and other diseases [1]. When prednisone is

* Corresponding author at: School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning, Guangxi 530008, China.
E-mail address: lixiaoyan73515@163.com (X. Li).

https://doi.org/10.1016/j.jcis.2018.05.030
0021-9797/

included in cosmetics, it leads to an improvement in the smoothness and texture of skin. However, the long-term use of these hormone-based cosmetics can lead to hormone dependence in conjunction with other side effects, which can lead to metabolic disorders or even cancer [2–4]. Therefore, The Hygienic Standard for Cosmetics published by Health Ministry of People's Republic of China in 2007 and EU Cosmetic Regulations [5] have clearly specified that the glucocorticoids are prohibited substances in cosmetics.

Currently, glucocorticoids in cosmetic samples are commonly detected by high performance liquid chromatography (HPLC) [6], thin layer chromatography [7], capillary electrophoresis [8], gas chromatography-mass spectrometry [9], and liquid chromatography-mass spectrometry [10–12]. However, these methods are often time consuming, complicated, and require large amounts of solvents and reagents. Thus, the selection of an appropriate sample preparation method is the key to efficient analysis of complex samples.

Surface molecularly imprinted solid-phase extraction (SMISPE) is an important sample pretreatment technique. Compared with traditional separation methods, SMISPE offers better selectively for substrates, and are easy to prepare. In this study, prednisone molecular capture (PS-MC) is a new SMISPE material, and is designed and synthesized by using surface molecular imprinting technology [13–18] with multi-walled carbon nanotubes (MWCNTs) [19–24]. Fig. 1 depicts the preparation process for the PS-MC. PS-MC has many characteristics of molecularly imprinted polymers, such as special adsorption and separation selectivity for template molecules. At the same time, PS-MC also has the characteristic of simple solid phase extraction separation [25,26], after finished the identification and adsorption of the template molecules, it can be removed directly from the sample matrix without the need for high speed centrifugation or magnetic separation. So using PS-MC can simplify the experimental steps, save time, and also save costs as the solid phase extraction material can be recycled.

2. Experimental

2.1. Chemicals

The polyethylene filter plate (plate) was purchased from Shanghai Chu Analysis Instrument Co. Ltd., Shanghai, China. MWCNTs were purchased from Pioneer of Nano Mstar Technology Ltd., Jiangsu, China (95%). Prednisone (97.5%) and clobetasol propionate (99.9%) were purchased from Wuhan Beierka Bio Pharmaceutical Co. Ltd., Wuhan, China. Hydrocortisone (99.0%) and dexamethasone (99.0%) were purchased from the Milky Way Hubei New Chemical Co. Ltd., Hubei, China. Trichloromethane, acetonitrile, aqueous, methanol, ethanol, and N,N-dimethylformamide were purchased from Chengdu Kelong Chemical Reagent Factory Co., China. Tetraethoxysilane (TEOS) was purchased from Tianjin Kermel Chemical Reagent Co. Ltd., Tianjin, China. 3-Aminopropyltriethoxysilane (APTES) was purchased from Shanghai Ruiyong Biotechnology Co., Ltd., Shanghai, China. All reagents used were of analytical or HPLC grade. The cosmetic samples were randomly purchased from supermarkets in Nanning (Guangxi, China).

2.2. Instrumentation and HPLC conditions

Scanning electron microscopy (SEM) was performed using SUPRA 55 Sapphire field emission scanning electron microscope (equipped with OXFORD X-MaxN51-XMX1004; Carl Zeiss, Germany). The Fourier-transform infrared (FT-IR) spectra were recorded using a Magna IR550 (II) type spectrophotometer (Nicolet, USA). The ultraviolet–visible (UV–vis) absorption spectra were recorded using a UV-1800 spectrophotometer (Suzhou Shimadzu Corporation). Thermogravimetric analyses (TGA) were recorded using the TG209F1 thermogravimetric analyzer (Netzsch, Germany). The specific surface area and pore diameter of the products were determined using the NOVE2000e Surface Area and Pore Size Analyzer (Quantachrome, USA).

HPLC analyses were performed using an Agilent 1260 HPLC equipped with a G1314B variable wavelength UV–vis detector, a G1316A column oven, and a G1311C quat pump. A Phenomenex Gemini C18 (5 μm particle size, 250 mm × 4.6 mm) analytical column was used for the separation of analytes. The mobile phase was acetonitrile/water (30:70, v/v), at a flow rate of 1.0 mL/min at 35 °C. The injection volume was 10 μL, and the wavelength of the detector was monitored at 240 nm.

2.3. Preparation of PS-MC

2.3.1. Preparation of plate@MWCNTs

To placed four pieces of polyethylene filter plate (plate) in a jar 0.1000 g of MWCNTs and 10 mL of N,N-dimethylformamide were added and placed under ultrasonic vibration for 15 min. The plates were then dried in a dry oven at 50 °C for 30 min. The trial was repeated for six times. Then, the plate was coated with MWCNTs (plate@MWCNTs), and that as the internal support for molecular capture.

2.3.2. Preparation of molecular and non-molecularly imprinted membranes (plate@MWCNTs@MIPs and plate@MWCNTs@NIPs)

Prednisone (0.2000 g), APTES (1.8 mL), and trichloromethane (30 mL) was added into a beaker and then underwent a ultrasonic vibration for 3 min. Then, four pieces of plate@MWCNTs were submerged in the mixture and the beaker was kept in the dark for 8 h. During this time, APTES bound to prednisone by hydrogen bonding to form a prepolymerization complex substance. Subsequently, 4.5 mL of TEOS, 1 mL of ammonia, and 10 mL of anhydrous ethanol were added and dispersed by stirring. The mixture was transferred to a three-necked flask, stirred, and reacted at 30 °C for 15 h under a nitrogen atmosphere to form a molecular imprinted membrane (plate@MWCNTs@MIPs) containing prednisone on the surface of the support. After reaction, the product was washed with methanol/glacial acetic acid (v/v, 8:2 or 9:1). The product was extracted by Soxhlet extraction to remove the template molecules, and washed repeatedly with methanol and air-dried naturally to afford plate@MWCNTs@MIPs.

The non-molecularly imprinted polymers (plate@MWCNTs@NIPs) were synthesized in the same manner as above without the addition of a prednisone template.

2.4. Characterization of molecular capture

The particle size, morphology, and composition of the plate, plate@MWCNTs, plate@MWCNTs@MIPs, and plate@MWCNTs@NIPs were studied by field emission scanning electron microscopy (FESEM) and energy dispersion spectra (EDS). The chemical structure of the polymers was investigated by Fourier transform infrared spectroscopy (FT-IR) and the thermal stability by thermogravimetric analysis (TGA).

2.5. Binding experiments

The binding experiments were performed with both plate@MWCNTs@MIPs and plate@MWCNTs@NIPs for comparison. In a typical procedure, four pieces of plate@MWCNTs@MIPs and plate@MWCNTs@NIPs were put into a wide-mouth bottle to which 10 mL of prednisone solution (1 mg/mL) was added. The mixture was covered and incubated for 2.5 h. PS-MC which had reached