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Cu- and S- @SnO_2 nanoparticles loaded on activated carbon for efficient ultrasound assisted dispersive μSPE-spectrophotometric detection of quercetin in *Nasturtium officinale* extract and fruit juice samples: CCD-RSM design

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ABSTRACT

A simple, rapid, and efficient method of dispersive micro solid phase extraction (D-μ-SPE) combined with UV–Vis spectrophotometry via ultrasound-assisted (UA) was applied for the determination and preconcentration of quercetin in extract of watercress (*Nasturtium officinale*), fruit juice and water samples. The sorbent in this method was synthesized by doping copper and sulfide into the tetragonal structure of SnO_2-nanoparticles (Cu- and S- @SnO_2-NPs) and subsequently loading it on activated carbon (AC). The D-μ-SPE parameters with direct effect on the extraction efficiency of the targeted analyte, such as sample pH, volume of eluent, sorbent mass and ultrasound time were optimized using central composite design method. Under optimized conditions, the calibration graph for quercetin was linear in the range of 20–4000 ng mL^{-1}; the limit of detection and quantitation were 4.35 and 14.97 ng mL^{-1}, respectively and the enrichment factor was 95.24. Application of this method to analyze spiked extract, fruit juice and water samples resulted in acceptable recovery values ranging from 90.3% to 97.28% with intra-day and inter-day relative standard deviation values lower than 6.0% in all cases. Among the equilibrium isotherms tested, Langmuir was found to be the best fitted model with maximum sorption capacity of 39.37 mg g^{-1}, suggesting a homogeneous mode of sorption for quercetin.

1. Introduction

Watercress (*Nasturtium officinale*) is a semi-aquatic fast-growing plant belong to Brassicaceae family which show distinguished health-promoting effects [1]. Raw watercress leaves known as salad greens and can steamed and consumed as a normal processed vegetable [2]. Watercress contains relatively large amount of vitamins C and provitamin A, folic acid, iodine, iron, protein and especially calcium and sulphur compounds which assign to its characteristic odour and cause its nutritional benefits [3,4] and usage in daily diet linked with reduced risk of chronic diseases including different types of cancer [4–6]. A previous study reported p-coumaric acid, quercetin-3-O-sophoroside and isorhamnetin-O-hydroxyferuloylhexoside-O-hexoside as the most abundant phenolic compound in wild watercress [7]. Flavonoids have higher value with respect to than phenolic acids assign to this extracts high contents of isorhamnetin and quercetin and lower content of kaempferol [7].

Quercetin (structure inset in Fig. S1) is the most active compound in flavone family, widely occurring in the leaves, fruits, and flowers of plants specifically watercress [8]. Quercetin is now the topic of interest due to its various bioactivities such as inoxidability, antiviral and antitumor property, and the ability to adjust the immune function [9]. Because of the complexity of the sample matrices, the structural similarity to other flavonols, and the existence of quercetins in nature at low concentrations, selective sample preparation methods are necessary prior to instrumental analysis. Preconcentration and/or separation of frequently is undertaken by solid phase extraction (SPE) [10,11], which expected to be effective for cleaning the different samples with at least cost and lowest time [12] Luckily, several other cleanup methods based on solid phase microextraction in different operational method via versatile sorbents were described for trace analysis [13–17]. Although dispersive micro solid phase extraction (D-μ-SPE) is considered as one

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of the most powerful cleanup technologies and have reports on application of D-μ-SPE in the analysis of quercetin was described.

Metal–oxide NPs are nominated as extractants for various compounds at trace levels in D-μ-SPE method [18,19]. Without any doubt, the use of metal–oxide NPs in D-μ-SPE is among the most important applications of these materials in analytical science. Metal–oxide NPs such as Cu- and S- @SnO_2-NPs loaded on activated carbon (AC) are suitable candidates for D-μ-SPE, due to their large surface area and the ability to establish π–π interactions as well as excellent Van der Waals and hydrogen bounds interactions with other molecules. However, their chemical, mechanical and thermal stability need to be studied further. The qualitative and quantitative analyses of food color was undertaken by approaches including chromatography [20,21], spectrophotometry [22–24], mass spectrometry [25], differential pulse polarography [26] and capillary electrophoresis [27] and amongst spectrophotometric based technique is acceptable alternative chemical analysis method via supplying acceptable precision and accuracy using lower cost compared to other techniques.

The shortcomings of traditional extraction technologies trigger food and chemical industries to find "green" separation techniques with less solvent and energy consumption [28,29]. Among all other options, ultrasound assisted extraction (UA) may be one of the most widely explored on both a laboratory and an industrial scale [30]. Ultrasound-assisted extraction (UA) technology is receiving considerable attention due to its beneficial properties, including high extraction efficiency, high reproducibility, low time and solvent consumption, easy operation, low cost and low pollution to environment [31,32].

The procedure is carried out under the synergistic effects of vibration, ultrasound action and heating, which greatly improves extraction efficiency, accelerate extraction process and enhance sample throughput. The new approach offers two improvements for D-μ-SPE [33,34] i.e. the use of the Cu- and S- @SnO_2-NPs-AC as a D-μ-SPE material combined with UV–Vis via a simple ultrasound-assisted (UA-D-μ-SPE-UV–Vis) for the determination of quercetin in extract and fruit juice samples.

in the method mentioned in the foregoing, the experimental variables, such as the eluent type and volume, pH and sonication time of the extraction efficiency were optimized traditional method known one at a time (OVAT) [35,36], which generally gives misleading results and is inefficient for optimizing experimental variables [37], while suffer from knowledge for expression on interaction among variable and consume large extent of reagent and times.

In our previous paper [38–41], we developed several rapid and reliable methods of organic compounds determination in water and wastewater samples. These studies were mainly focused on water, urine and plasma samples. Current report summaries effective sample pretreatment procedures based on UA-D-μ-SPE, where the method is validated by determining the amount of quercetin in 100, 200, 300 and 400 ng mL^{-1} of artificially spiked samples of watercress extract, apple and grape fruit juice in water samples. To the best of our knowledge, this is the first report on the determination of quercetin in the extract of watercress using UA- D-μ-SPE by UV–Vis.

2. Materials and methods

2.1. Standard solutions and chemicals

Tin (II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$), Tin (IV) chloride ($SnCl_4$), thioacetamide (CH_3CSNH_2) and ammonium acetate (NH_4 (CH_3COO)) were purchased from Scharlau Company. Quercetin was purchased from Sigma–Aldrich (Steinheim, Germany). Methanol, ethanol, acetonitrile, acetone, dimethylformamide, tetrahydrofuran (analytical-grade), cupper (II) acetate ($Cu(CH_3COO)_2$ and activated carbon were purchased from Merck (Darmstadt, Germany). The water used for mobile phase was double distilled deionized which was produced by a Milli-Q system (Millipore, Bedford, MA, USA). A stock standard solution of quercetin (100 mg L^{-1}) was prepared in methanol. The working solutions were prepared by appropriate dilution of the stock solution with double distilled/deionized water. All of the standard solutions were stored in the dark at 4 °C and brought to ambient temperature just prior to use.

2.2. Instrumental characterization and software

The morphology of the nanoparticles were observed by field emission scanning electron microscopy (FE-SEM, Ziess) under an acceleration voltage of 15.00 KV. The atomic composition of the Cu- and S- @SnO_2-NPs-AC was analyzed by energy-dispersive X-ray spectrometry (EDX) using an Oxford INCA II energy solid state detector. X- ray diffraction (XRD, Philips PW 1800) was preformed to characterize the phase and structure of the prepared nanoparticles using $Cu_{K\alpha}$ radiation (40 KV and 40 mA) at angles ranging from 10 to 80°. The ultrasound-assisted extraction was carried out in an ultrasonic bath system with a frequency of 40 kHz (Tecno-GAZ SPA Ultrasonic System, Bologna, Italy). The response surface regression was used to analyze the experimental data using Statistica Version 10.0 software (Stat Soft Inc., Tulsa, USA). Two dimensional contour plots were developed. All processing trials were conducted in triplicate.

2.3. Sampling and sample preparation

Watercress (*Nasturtium officinale*) plant was harvested from Kakan region located in Yasuj, Iran. A voucher specimen (voucher number) was deposited at the herbarium of the Department of Botany, Yasouj University, Yasouj, Iran. Dried Watercress (*Nasturtium officinale*) (100 g) was mixed with methanol (80%) at room temperature (25 ± 2 °C) for 72 h. The extract was then filtered and the residue was re-extracted using fresh 80% methanol for 24 h. To concentrate the sample, a rotary under low pressure at 45 °C was used to evaporate methanol [42].

The dried extract (0.01 g) was dissolved in methanol (15 mL) under 40 kHz, 130 W, and 45 °C in an ultrasonic bath device for 10 min; thereafter the dissolved extract was centrifuged at 6000 rpm for 15 min. After filtering through a filter paper and a 0.45 μm membrane filter (Millipore), the extract was diluted with double-distilled water to 1:30. Moreover, the proposed method was applied to determine food colorants in two fruit juice samples (apple and grape juice) produced in Yasuj, Iran. All the samples were purchased from local supermarkets. Fresh juice samples were centrifuged at 4000 rpm for 15 min. The supernatant was then filtered through a 0.45 μm membrane filter and diluted with double-distilled water to 1:30. pH was set at 3.5 using concentrated HCl and/or NaOH following ultrasonication [43].

2.4. Preparation of the Cu- and S- @SnO_2-NPs-AC

The reaction solution for synthesis of the Cu- and S- @SnO_2-NPs-AC was prepared as follows: 8.0 mL of ammonium acetate (1.0 mol L^{-1}) solution was mixed with 8.0 mL of 0.5 mol L^{-1} tin (II) chloride dehydrate ($SnCl_2{\cdot}2H_2O$) solution. 10.0 mL of $SnCl_4$ (8% v/v) solution and 10.0 mL of 0.4 mol L^{-1} thioacetamide (CH_3CSNH_2) solution were subsequently added to the mixed solution under sonication, followed by the addition of deionized water to make a total volume of 100 mL. The prepared reaction solution was transferred to an oven at 50 °C for 24 h. After 24 h, 1.0 mL of 0.002 mol L^{-1} copper acetate solution was added to 25 mL of the reaction solution drop by drop to obtain the Cu- and S-@SnO_2-NPs. The obtained Cu- and S- @SnO_2-NPs was then dispersed in 200 mL of de-ionized water in an Erlenmeyer flask to make an insoluble suspension. Finally, the homogenous deposition of the Cu- and S- @SnO_2-NPs on activated carbon (AC) was carried out by adding 12.0 g of AC to the prepared Cu- and S- @SnO_2-NPs suspension while being strongly stirred for 18 h at 25 °C. The fabricated Cu- and S- @SnO_2-NPs-AC was then filtered, washed several times by de-ionized water, dried at 50 °C for 5 days and finally used as a sorbent in extraction experiments.