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Curcumin nanoparticles combined with cloud point extraction for citrate determination in food and drug samples

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ABSTRACT

In the current work, the enriched curcumin nanoparticles (CURNs) in nonionic surfactant phase in the presence of Fe^{3+} has been utilized for colorimetric recognition of citrate ions. The absorption intensity of CURN-Fe^{3+} complex transferred into the surfactant rich phase is decreased upon the addition of citrate ion owing to its interaction with citrate ions and consequently the formation of new complex (CURN-Fe^{3+}-citrate). This decrease in the absorption intensity of surfactant rich phase is proportional to the citrate concentration and was utilized for colorimetric sensing of citrate ions. The reaction conditions such as pH of the sample solution, concentration of Fe^{3+}, electrolyte and CURNs were appraised and optimized. Under the optimum experimental conditions, the proposed method demonstrated two linear calibration intervals in the concentration ranges of 3–100 ng mL^{-1} and 100–600 ng mL^{-1} of citrate with a detection limit of 1.7 ng mL^{-1}. The relative standard deviations (RSD) of 2.91% and 0.97% for 8 replicated measurements of 10 ng mL^{-1} and 400 ng mL^{-1} of citrate, respectively, indicate that developed method has good reproducibility. Eventually, the practical efficiency of the developed method was demonstrated to the analysis of citrate in lemon juice and pharmaceutical samples with satisfactory results.

1. Introduction

Citric acid as a nontoxic organic acid is found in citrus fruits and is produced commercially during fermentation of some organic compounds such as carbohydrates. Citric acid and its salts are widely utilized in foods, pharmaceuticals, cosmetics, cleaning and chelating agents. They are used as food preservatives and flavoring, preventing yeast, mold growth and acidifier in food industry. Determination of citrate concentration is also a key factor in assessing the quality of agricultural, food and some of other products [1–6]. Up to now, numerous methods such as electrochemical [1,3,4], optical [5–7], luminescence [8,9], capillary zone electrophoresis [10], enzymatic [11] and flow-injection chemiluminescence [12] have been developed to determine the concentration of citrate. However, because of inadequate sens itivity and matrix interferences in most of the analytical techniques, direct determination of analytes without separation and preconcentration process is difficult. Accordingly, the separation and preconcentration of some analytes at trace concentration is considered as a critical step. Cloud point extraction (CPE) as a green extraction technique has been used for the preconcentration and separation of analytes and was first introduced by Watanabe and Tanaka [13].

Compared to other techniques for analyte separation/preconcentration, CPE has the desired advantages of simplicity, low cost, low toxicity and being environmental friendly. When the temperature of aqueous solution containing surfactant, above its critical micellar concentration (cmc), is increased to certain temperature (cloud point temperature) of surfactant, the solution becomes turbid and separates into two distinct liquid phases: a surfactant-rich phase with the small volume and a dilute phase with a surfactant concentration close to the cmc. Under this condition, the hydrophobic compounds (organic species or inorganic species after complex formation) that are present in the samples, after interaction with micelles, can be preconcentrated in the surfactant-rich phase of a micellar solution [14].

Recently, there is also a raising research interest in application of nanomaterials in micelle mediated systems due to their many fascinating and remarkable characteristics that can help to improve the efficiency of micelle mediated systems [15–17]. Various types of nanomaterials such as gold, silver, diamond and titanium oxide have been utilized in micelle mediate systems for preconcentration and determination of some analytes [17–19]. We have recently reported the noticeable ability of silver and curcumin nanoparticles in micelle mediated systems for colorimetric determination of copper and sulfide ions, respectively [15,20].

Curcumin, [(E,E)-1,7-bis (4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione], is natural diphenolic compound which has

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been recognized as a naturally occurring yellow pigment and component of the spice, turmeric. It is derived from the dried root of the rhizome *Curcuma longa*. Curcumin exhibits different tautomeric forms: 1,3-diketo form and keto-enol tautomeric forms in which the second ones are more stable than the former in both solution and solid state [21]. Curcumin shows antioxidant, antimicrobial, anticarcinogenic, wound healing and anti-inflammatory properties and can readily chelate the metal ions to form the complexes [22,23]. The complexing ability of curcumin toward iron ion as an iron chelator has been recognized and utilized in numerous studies. The chelating ability of curumin for iron binding is comparable to nitrilotriacetic acid and many of other iron chelators [24,25]. Moreover, the ability of curcumin to reduce the risk of Alzheimer disease has been related to its iron chelating properties [26]. Despite the numerous advantages of curcumin, it has poor solubility in aqueous solutions which can limit some of its applications; however, nanonization is one of the effective methods that could solve this drawback [27–29].

In this article, we present a new method for the effective colorimetric determination of citrate ions in food and drug samples using curcumin nanoparticles (CURNs) in CPE method. The complex of CURN-Fe(III) is enriched into the surfactant-rich phase of CPE and exhibits an absorption peak at $\lambda = 416$ nm, but upon the addition of citrate ion, transfer of CURN-Fe(III) into the surfactant-rich phase is decreased due to complex formation between Fe^{3+} and citrate ion. Hence, the decrease in absorbance intensity of CURN-Fe(III) in surfactant-rich phase at $\lambda = 416$ nm was used as an analytical signal for spectrophotometric determination of citrate ions. The effects of different parameters such as pH of solution, concentrations of CURNs, Fe^{3+}, surfactants and electrolytes, equilibrium temperature and incubation time on the method performance was investigated and the best experimental conditions were chosen to achieve a sensitive and selective method.

2. Experimental

2.1. Instrumentation

The spectrophotometric measurements and recording absorption spectra were performed by GBC UV–visible spectrophotometer model Cintra 101 (Sydney, Australia) using 1 cm glass cuvettes. TEM images were obtained with a transmission electron microscope (Zeiss-EM10C-80 KV, Germany).

A Metrohm pH-Meter model 632 with a combined glass electrode ((Herisau, Switzerland) was used for the pH measurements. A thermostat bath model Colora (England) maintained at the desired temperature was used for the cloud point temperature experiments. An ultrasound bath DSA 100-SK2, 100 W power, 40 kHz frequency (China) was utilized for fabrication of CURNs. A Heidolph rotary evaporator model Labrota 4000 (Germany) was applied for removing the solvent during the fabrication of CURNs.

2.2. Reagents

All chemicals were of analytical grade and doubled distilled water was used throughout. A 1000 μg mL^{-1} stock solution of citrate ion was prepared by dissolving 0.1132 g of mono sodium citrate (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. A stock solution of 1000 μg mL^{-1} of Fe^{3+} ion was prepared by dissolving 0.484 g of the $FeCl_3 \cdot 6H_2O$ (Merck) in 1 mL of HCl (Merck) and diluting with water in a 100 mL volumetric flask. More diluted solutions were prepared daily using this stock solution. 0.5 mol L^{-1} of NaCl and 5% (v/v) of Triton X-100 were used. Formate buffer pH 3.5 was prepared by the addition of NaOH (1.0 mol L^{-1}) solution to 0.01 mol L^{-1} of formic acid and adjusting the pH to 3.5 using a pH meter.

2.3. Synthesis of CURNs

The CURNs were fabricated by our formerly reported method for the modification of the technique described by Bhawana et al. [20,28]. The fabrication procedure was represented as follows: the organic phase was prepared by dissolving 125 mg of curcumin in 25 mL of dichloromethane. For preparation of aqueous phase, 10 mL of Triton X-100 5% (v/v) was added to 90 mL of boiling water. Subsequently, 2 mL of organic phase was added drop wise to the above boiling aqueous phase (about 10 drops/min) under ultrasonic conditions, with an ultrasonic power of 100 W and a frequency of 40 kHz. After that the sonication

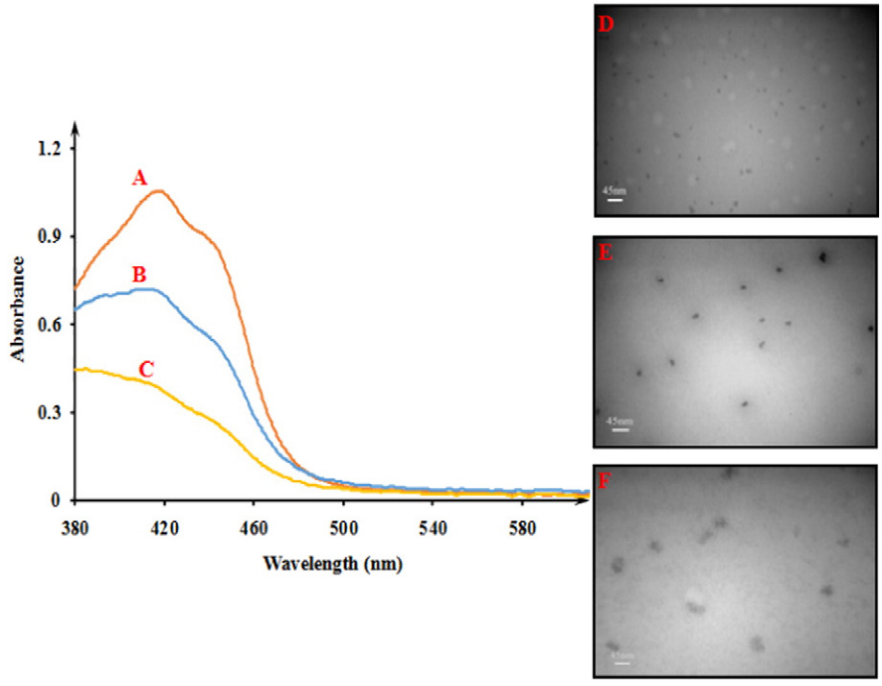

Fig. 1. UV–vis spectra of the extracted CURNs using CPE: (A) in the absence of citrate and Fe^{3+}, (B) in the presence of Fe^{3+} and (C) in the presence of both citrate and Fe^{3+} and the corresponding TEM images of CURNs in micellar solution, (D) in the absence of Fe^{3+} and citrate, (E) in the presence of Fe^{3+} and (F) in the presence of both citrate and Fe^{3+}.