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Colorimetric sensing of oxalate based on its inhibitory effect on the reaction of Fe (III) with curcumin nanoparticles

Nahid Pourreza [a,*], Neda Lotfizadeh [a], Hamed Golmohammadi [b]

[a] Department of Chemistry, Faculty of Science, Shahid Chamran University of Ahvaz, Ahvaz, Iran
[b] Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

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ABSTRACT

In this research, a new colorimetric method for the determination of oxalate using curcumin nanoparticles (CURNs) in the presence Fe (III) is introduced. The method is based on the inhibitory effect of oxalate ion on the reaction of (CURNs) with Fe (III) in acidic media. This reaction was monitored by measuring the increase in absorbance of CURNs-Fe^{3+} complex in the presence of oxalate ion at 427 nm. The effect of different parameters such as the pH of the sample solution, concentration of Fe (III), concentration of CURNs and the reaction time was examined and optimized. Under optimum experimental conditions, the absorption intensity was linear with the concentration of oxalate in the range of 0.15 to 1.70 μg mL^{-1}. The limit of detection (LOD) was 0.077 μg mL^{-1} and the relative standard deviations (RSD) for 8 replicate measurements of 0.40 and 1.05 μg mL^{-1} of oxalate were 4.20% and 2.74%, respectively. The developed method was successfully employed to the determination of oxalate in water, food and urine samples with satisfactory results.

1. Introduction

Oxalate ion, is commonly synthesized through the incomplete oxidation of carbohydrates and is also generated during some biological and industrial processes. It is naturally found in many plants such as spinach, mushroom, celery, rhubarb, beet leaves and so forth. Knowledge of the oxalate concentration in biological fluids such as blood and urine can be helpful in the investigation, diagnosis and medical management of various clinical disorders/diseases including chronic renal failure, primary hypemxaluria, intestinal malabsorption, nephrolitiasis, steatorrhoca and ileal disease [1–4]. On the other hand, owing to the low solubility of oxalates (e.g. calcium oxalate) and subsequently their precipitation on the surface of evaporation units, reactors, pipelines, pumps, they could lead to severe operational problems [5]. Because of this, accurate determination of oxalate in different food, biological and environmental matrices has been of strong interest.

To date, a variety of methods have been developed for the determination of oxalate, including titration [6], amperometry [7,8], capillary electrophoresis (CE) [9], gas chromatography [10], high performance liquid chromatography (HPLC) [11], spectrophotometry [12,13], ion chromatography [14], fluorescence detection [15], amperometric biosensor [16] and enzymatic analysis [17]. Some of the aforementioned analytical techniques for the determination of oxalate require expensive and sophisticated equipments and also suffer from the use of toxic and expensive reagents, insufficient sensitivity, and matrix interferences. Consequently, there is a significant demand to develop a sensitive, selective, economical and environmentally friendly approach for the detection of oxalate in complex matrices.

Curcumin or [(E,E)-1,7-bis(4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione], as an active intergradient of turmeric, is a yellow natural hydrophobic polyphenol pigment that is isolated from *Curcuma longa*. Curcumin is greatly consumed as a seasoning, coloring and preserving agent in food, drugs and cosmetics. It exhibits the extraordinary properties such as antioxidant, antibacterial, anti-inflammatory, anticarcinogenic and wound healing [18–22]. The chelating ability of curcumin to form complexes with some metal ions such as iron, zinc and copper has also been reported in several studies [23]. Despite having numerous advantages, the poor water solubility of curucumin limits bioavailability and its application. To overcome this limitation, nanonization can be considered as an effective way.

The potential use of curcumin nanoparticles (CURNs) for (bio) chemical sensing have been reported in several studies [24–26]. We have previously shown the application of CURNs as efficient chemoprobes for quantitative determination of different analytes [27,28].

Herein, we have developed a colorimetric sensing method for quantitative determination of oxalate using CURNs in the presence of Fe (III) ions. The absorption intensity of CURNs is decreased by the addition of Fe(III) ions because of complex formation (CURNs-Fe(III)), but upon adding oxalate ions due to its high affinity toward Fe(III), the reaction is inhibited and the absorption intensity is restored again. This increase

* Corresponding author.
E-mail address: npourreza@scu.ac.ir (N. Pourreza).

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in the absorption intensity of CURNs-Fe(III) is proportional to the oxalate concentration and was utilized as analytical signal (ΔA) for the spectrophotometric determination of oxalate ions. In order to enhance the sensitivity and selectivity of the developed method, the effects of various parameters such as pH of sample solution, concentrations of HCl, CURNs, Fe(III), reaction time and tolerance limit of a variety of possible interferences on the performance of the method for oxalate sensing were evaluated.

2. Experimental

2.1. Instrumentation

Absorption spectra were recorded by a GBC UV–vis spectrophotometer model Cintra101, (Australia) with 1 cm glass cuvettes. A Jenway 6705 single beam spectrophotometer (England) with 1.0 cm glass cell was used to measure the absorbance at a fixed wavelength. TEM images were performed by a Zeiss- EM10C-80 KV transmission electron microscope (Germany). The pH measurements were accomplished by a digital pH-Meter model 632, Metrohm (Switzerland) with a combined glass electrode. An ultrasound bath DSA 100-SK2, 100 W power, 40 kHz frequency (China) was employed for fabrication of CURNs. A Heidolph rotary evaporator model Labrota 4000 (Germany) was applied for the removal of solvent.

2.2. Reagents

All chemicals were of analytical grade and doubled distilled water was used for the preparation of the solutions. A stock solution of oxalate ion (1000 μg mL^{-1}) was prepared monthly by dissolving 0.1523 g of $Na_2C_2O_4$ (Merck, Darmstadt, Germany) in water and diluting to 100 mL in a volumetric flask. More diluted solutions were prepared daily using this stock solution. A stock solution of 1000 μg mL^{-1} of Fe(III) ion was prepared by dissolving 0.484 g of the $FeCl_3.6H_2O$ (Merck) in 1 mL of HCl (Merck) and diluting with water in a 100 mL volumetric flask. A 5% (*v*/v) of Triton X-100 (Merck) was prepared by diluting 50 mL of the reagent to 1000 mL.

2.3. Synthesis of CURNs

The CURNs were prepared according to our previously reported method [27,28] as follows: 125 mg of curcumin was completely dissolved in 25 mL of dichloromethane to prepare the organic phase. The aqueous phase was prepared by adding 10 mL of Triton X-100 5% (*v*/v) to 90 mL of hot water (70–80°C). Afterwards, 2 mL of organic phase was slowly and dropwise introduced into the aqueous phase (about 10 drops/min) under ultrasonic conditions, with an ultrasonic power of 100 W and a frequency of 40 kHz. The sonication was then continued for 20 min followed by stirring on a magnetic stirrer at room temperature for 20 min until a yellow color was obtained. In order to ensure the complete removal of dichloromethane, this solution was finally placed in a rotary evaporator under reduced pressure. The CURNs solution was stored in a brown bottle for further use. The prepared CURNs are stable for more than six months.

2.4. General Procedure for Determination of Oxalate

The experimental procedure for colorimetric determination of oxalate was performed as follows: 2.0 mL of the synthesized CURNs solution, 1.0 mL of 10 mg L^{-1} of Fe (III) solution, 1.75 mL of 0.1 mol L^{-1} HCl and aliquots of oxalate solution (so that its final concentration would be in the range of 0.15–1.70 μg mL^{-1}) were transferred to a 25 mL volumetric flask and diluted to the mark with water. The

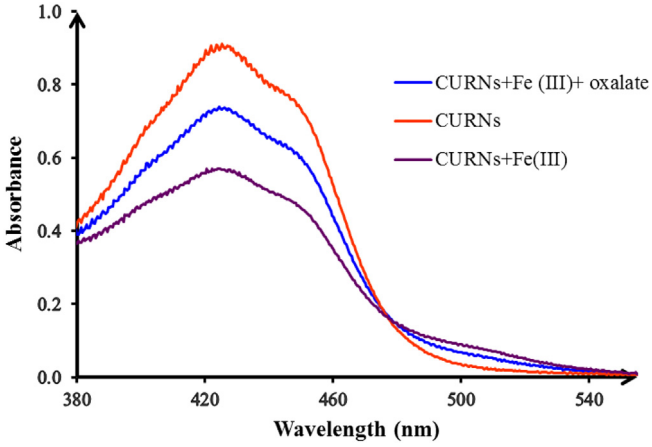

Fig. 1. UV–vis spectra of the CURNs in the absence Fe (III), presence of Fe (III) and in the presence of both Fe (III) and oxalate ion.

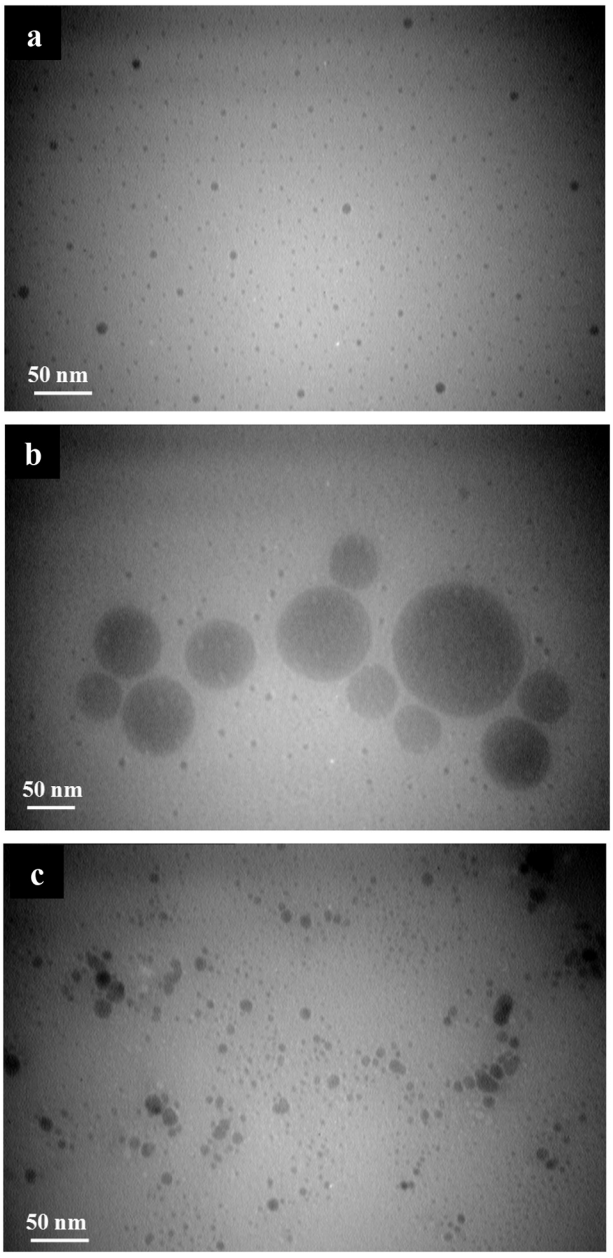

Fig. 2. (a) TEM images of CURNs in the absence of Fe (III) (b) in the presence of Fe (III) and (c) in the presence of both oxalate and Fe (III).