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Novel metal nanoparticle-enhanced fluorescence for determination of trace amounts of fluoroquinolone in aqueous solutions

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ABSTRACT

Metal-enhanced fluorescence of fluoroquinolones (FQs) was first observed in aqueous solutions. In addition, a new type of silver nanoparticles (AgNP) was synthesized with simple and easy synthetic processes and environmentally friendly compounds. The effects of different concentrations of AgNPs on the fluorescence behaviours of ciprofloxacin (CIP), enrofloxacin (ENR) and lomefloxacin (LMF) in aqueous solutions were investigated, respectively. The experimental results demonstrated that the fluorescence peak shapes and the locations of the features in the excitation and emission spectra for each FQ that was mixed with AgNPs were almost the same as those of the standard FQs. An enhancement or quenching of the fluorescence can also be observed, depending on the exact conditions. Compared with the identical control samples that lack AgNPs, the fluorescence of each FQ in aqueous solutions was greatly enhanced by AgNPs with concentrations at a volume ratio of 5%. Moreover, at the optimum AgNP concentration, novel sensitive fluorometric methods for the separate determination of trace amounts of CIP, ENR and LMF in aqueous solutions were established. Under optimal experimental conditions, the linear dynamic ranges for the determination of CIP, ENR and LMF concentrations varied from 0.025 to 1.0 mg L^{-1}, 5.0 to 160 ng L^{-1} and 0.01 to 0.8 mg L^{-1}, and the limits of detection were 90, 5 and 6 ng L^{-1}, respectively; the relative standard deviation was less than 1.2% (n = 9). The experimental recovery results for the determination of CIP, ENR and LMF in aqueous solutions ranged from 99% to 102%, 90% to 103% and 92% to 107%, respectively. Compared with the established method in which no AgNPs were added, the quantitation limits of the silver nanoparticle-enhanced fluorometric methods were approximately 2-fold lower for CIP, 2.6-fold lower for ENR and 4-fold lower for LMF. Significantly, the novel silver nanoparticle-enhanced fluorometric methods were successfully applied to directly determine CIP, ENR and LMF concentrations in pharmaceutical preparations, demonstrating the methods' advantages of simplicity, sensitivity and low cost.

1. Introduction

Antibiotics are an important group of pharmaceuticals and have been found in various compartments of the environment (e.g., soils, sewage and sludge as well as waters) due to the increase in their consumption [1–3]. The concern over the release of antibiotics into the environment is related primarily to the potential for the development of antimicrobial resistance among microorganisms [4,5]. According to reports, heavy use of antibiotics that have contaminated the aquatic environment has led to a significant increase in antibacterial resistance, which has had important consequences for public health [6]. Fluoroquinolones (FQs), the second generation of quinolone antibiotics, are a group of broad-spectrum anti-bacterial agents with a unique mechanism of action and wide clinical use [7,8]. To date, various analytical methods have been established for the determination of FQs and their derivatives, including capillary electrophoresis (CE) [9,10], spectrophotometry [11,12], liquid chromatography mass spectrometry [13], liquid chromatography-tandem mass spectrometry [14], and high-performance liquid chromatography (HPLC) [15–17]. However, most of the abovementioned methods are time-consuming, owing to the requirement of complicated and sophisticated instruments, or have limited sensitivity and selectivity for the determination of trace FQs in aqueous solutions. Fluorimetry could be a very simple, rapid and sensitive method for the detection of fluorophores at trace levels

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[18,19]. However, the detection of a fluorophores is usually limited by their quantum yield, the autofluorescence of the sample and the photostability of the fluorophores [20]. FQs can produce fluorescence because their molecular structure contains conjugated heterocycle. Due to their low quantum yield, the application of fluorimetry to the study of FQs has been limited. Thus, it is necessary to enhance the fluorescence intensities of FQs in aqueous solutions to reach higher sensitivities and a wider range of applications.

Metal-enhanced fluorescence (MEF) has exhibited promise for applications in fluorometric assays because of the wide use of molecular fluorescence measurement and devices in chemistry [21,22]. The MEF usually originates by the interactions of fluorophores with metallic nanomaterials and has been widely employed to enhance the fluorescence signals of fluorophores. In addition, the MEF could modify the spectral properties of the fluorophores, such as improved photostability and decreased lifetime [23,24]. In particular, to achieve MEF, many efforts have been devoted to the synthesis and characterization of stable dispersions of nanoparticles made of silver, gold, and other noble metals [25,26]. Among them, silver nanoparticles (AgNPs) have been widely studied due to their useful, optical, electrical and catalytic properties [27,28]. However, most traditional methods for the synthesis of AgNPs require a large amount of organic solvent during the synthetic reaction and for the separation and extraction procedures, which might cause secondary pollution problems [29–31]. In our previous studies, a special type of AgNP was synthesized using “green chemistry”. Moreover, a new fluorometric method using the MEF effect had been established for the determination of two kinds of tetracyclines in aqueous solutions [32]. Nonetheless, the development of enhancing fluorescence by exploring new and environmentally friendly nanoparticles is still lacking.

In this work, another new kind of AgNP was synthesized with synthetic processes that were simple and easy to operate and used raw materials that were environmentally friendly compounds. In addition, ciprofloxacin (CIP), enrofloxacin (ENR) and lomefloxacin (LMF), representing antibiotics with certain properties, were selected as model FQs. Thus, novel fluorometric methods based on the MEF of AgNPs were established for the direct determination of CIP, ENR and LMF in aqueous solutions, respectively. Moreover, under the optimum conditions, the contents of CIP, ENR and LMF in pharmaceutical preparations that were dissolved in water were separately determined utilizing the novel established silver nanoparticle-enhanced fluorometric method.

2. Materials and methods

2.1. Apparatus and reagents

Optical absorption spectra were obtained using a UV–visible spectrophotometer with a quartz cell of 1 cm path length at room temperature. All fluorescence spectra were recorded on a F-4600 fluorescence spectrophotometer (Hitachi Corporation, Japan), which was equipped with a xenon flash lamp (150 W) and single-grating monochromators as wavelength selection devices. The spectrofluorometer was controlled by F-4600 software to acquire and process the spectral data. Fluorescence measurements were performed using a standard $1 \times 1\ cm^2$ quartz cell. The fluorescence spectra were obtained with the following instrumental parameters: the excitation and emission slits were set to 5 nm, the scan speed was 1200 nm min^{-1}, and the PMT voltage was set at 700 V. In addition, the morphology and size of the obtained AgNPs were observed with a LEO-1530 scanning electron microscope (Zeiss, Germany). Moreover, powder X-ray diffraction (XRD, PANalytical B.V.) was also used to analyse the patterns of the AgNPs.

The CIP (C17H18FN3O3.HCl, purity > 94%), ENR ($C_{19}H_{22}FN_3O_3$ purity > 99%) and LMF (C17H19F2N3O3.HCl purity > 99%) were obtained from Sigma Aldrich and used without further purification. The stock solutions of each FQ compound were prepared by dissolving the compounds in ultrapure water. All of the solutions were stored in brown volumetric flasks at 4 °C and wrapped with aluminium foil to avoid possible photodegradation. The working solutions of CIP (0.60 mg L^{-1}), ENR (0.15 mg L^{-1}) and LMF (0.30 mg L^{-1}) were prepared by dilution of the stock solutions in ultrapure water before use. Sodium citrate (Guangdong Xilong Chemical Reagent Co., Ltd. China), β-cyclodextrin (β-CD, Sinopharm Chemical Reagent Co., Ltd. China) and silver nitrate (Shanghai Lingfeng Chemical Reagent Co., Ltd. China) were also used in these experiments.

2.2. Synthesis of AgNPs

On the whole, the AgNPs were prepared by the reduction of silver nitrate and sodium citrate with β-CD as the protecting reagent. In brief, the β-CD (1.0 g) was added to the silver nitrate solution (49 ml, 1.1 mmol L^{-1}), and then the mixture was heated to boiling. After that, the sodium citrate (1 ml, 38.8 mol/L) was added dropwise to the mixture within 2 min while stirring vigorously. The reaction proceeded for approximately 30 min while boiling. The morphology and size of the obtained AgNPs were determined using a LEO1530 scanning electron microscope.

2.3. Effect of AgNPs on the fluorescence behaviours of CIP, ENR and LMF in aqueous solutions

The working solutions of each FQ were diluted in a series of volume ratios (0%, 1.0%, 5.0%, 10%, 20%, 25%, 30%, 40%, 50%, 75%, and 100%) with the AgNPs in water, and 10 ml of 1.0 mg L^{-1} of each FQ was prepared with these mixtures. Then, the mixture of each FQ was separately placed into the fluorescence spectrophotometer for direct determination of their fluorescence intensities at the selected wavelength. The values of the fluorescence intensities represented the average behaviours shown by each FQ at the different volume ratios. All of the data were obtained at room temperature.

2.4. Determination of CIP, ENR and LMF in pharmaceutical preparations

Two kinds of each FQ were selected in this experiment, including CIP tablets and capsules, two ENR injections, and LMF ear drops and eye drops. For convenience, the CIP tablets and capsules were called A (0.25 g per tablet, Hangzhou Jingxin Pharmaceutical Co., Ltd. China) and B (0.25 g per capsule, Hangzhou Jingxin Pharmaceutical Co., Ltd. China), respectively. In addition, the two ENR injections were separately called C (0.10 g ml^{-1}, Sichuang Jixing Animal Pharmaceutical Co., Ltd. China) and D (25.0 mg ml^{-1}, Shanxi Ruicheng Kelong Veterinary Pharmaceutical Co., Ltd. China). The LMF ear drops and eye drops were called E (3.0 mg ml^{-1}, Wuhan Nuoan Pharmaceutical Co., Ltd. China) and F (3.0 mg ml^{-1}, Wuhan Nuoan Pharmaceutical Co., Ltd. China) respectively.

First, the measurement procedures for the CIP tablet and capsule were as follows. Ten tablets of A and ten capsules of B were selected and ground into their respective powders. Then, the powders of one tablet and one capsule were weighed accurately and then separately dissolved in a Tris-HCl (pH = 8, Solarbio) buffer solution. The solution of each medicine was then filtered, and the residue was washed several times and dissolved to the desired concentration with water. Finally, the working solutions of A and B, with the addition of a certain amount of AgNPs, were placed directly into the fluorescence spectrophotometer for the direct determination of their fluorescence intensities. Each experiment was conducted three times. All of the data were obtained at room temperature.

Second, the ENR injection measurements proceeded according to the following steps. A certain amount of C (1.0 ml) and D (1.0 ml) was separately added to ultrapure water to the total volume of 50 ml; these samples were further diluted with ultrapure water approximately 200-fold and 50-fold. The working solutions of C and D that contained a