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Determination of diclofenac sodium by resonance light scattering method using silver nanoparticles as probe

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ABSTRACT

A sensitive, simple and novel method was developed to determine diclofenac sodium (DS) using silver nanoparticles (AgNPs) as probe by resonance light scattering (RLS) technique. It was found that DS could quench the RLS intensity of AgNPs. Moreover, the decrease in RLS intensity was linearly correlated to the concentration of DS over the range of 0.01–2.0 μg mL^{-1}. DS can be measured in a short time (5 min) without any complicated or time-consuming sample pretreatment process. Parameters that affect the RLS intensities such as pH, concentration of AgNPs, reaction time, electrolyte concentration, and coexisting substances were systematically investigated and optimized. The results showed that the method had a very good selectivity and could be used conveniently for the determination of DS. The limit of detection (LOD) was 2.85 ng mL^{-1} (3σ), and the relative standard deviation (RSD) was less than 3.6% ($n = 6$). Possible mechanism for the RLS changes of AgNPs in the presence of DS was discussed and the method was successfully applied for the analysis of tablets and urine samples.

1. Introduction

Diclofenac sodium (DS) is an important non-steroidal anti-inflammatory drug that is widely used for the treatment of rheumatoid arthritis, osteoarthritis, musculoskeletal injuries and post-surgery analgesia in human medicine [1]. It has been measured by a variety of analytical techniques such as gas chromatography (GC) and high performance liquid chromatography (HPLC) [2,3], electrochemistry [4,5], fluorimetry [6–8] and spectrophotometry [9–11]. To develop a simple, sensitive, and high accuracy method for determination of DS has become increasingly important.

In recent years, gold/silver nanoparticles have received considerable interests for their unique optical and electrical properties. Generally, the optical properties of gold/silver nanoparticles are dominated by collective oscillation of electrons at surfaces (known as surface plasmon resonance) and any change to the environment of nanoparticles (surface modification, aggregation, medium refractive index, etc.) leads to colorimetric changes of the nanoparticles suspension [12]. Because of this unique optical property, gold/silver nanoparticles have been extensively used as probes for sensing various analytes, such as metal ions [13–15], organics [16,17], and pharmaceuticals [18]. This color of the small gold/silver nanoparticles mainly belongs to the localized surface plasmon resonance absorption. In addition, the large particles and the aggregates of small gold/silver nanoparticles exhibited strong resonance scattering and their color was related to the resonance scattering wavelength. The resonance light scattering intensity can be decreased or enhanced by addition of analyte and all that could be used for quantitative detection of analytes. Thus, another analytical method gaining importance is resonance light scattering (RLS), which is characterized by its high sensitivity, simple setup and convenient operation. RLS has been widely applied for the determination of different analytes including inorganic ions, organic compounds, biomacromolecules and pharmaceuticals [19–26]. However, there has not been any reports for determination of DS using AgNPs as probe by RLS technique.

The citrate-capped AgNPs have electronegative charged surface and can be dispersed from each other in the water symmetrically by the electrostatic repulsion, exhibiting yellow color for the surface plasmon resonance [27,28]. However, the presence of DS induces the aggregation of AgNPs, causing RLS intensity change of AgNPs suspension. It was found that the added DS could reduce the RLS intensity of the AgNPs in aqueous solutions and the decrease in RLS intensity was in proportion to the concentration of DS. Therefore, the novel method was developed to determine DS using AgNPs as probe by RLS technique. The proposed method has been used for the analysis of DS in tablets and urine samples with satisfactory results.

2. Experimental

2.1. Materials and Reagents

Diclofenac sodium, ibuprofen, p-hydroxybenzoic acid, phenylacetic acid, salicylic acid, diphenyl acetic acid and benzoic acid were purchased

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from Aladdin Chemical Reagent (Los Angeles, USA) and DS was used to prepare for 1.0 g L^{-1} standard stock solution and the standard working solution was prepared by diluting the stock solution to 10.0 μg mL^{-1}. Silver nitrate ($AgNO_3$) and sodium citrate were purchased from Tianjin Chemical Reagent Factory (Tianjin, China). Acetic acid, boric acid, phosphoric acid and sodium hydroxide were purchased from Xi'an Chemical Reagent Factory (Xi'an, China). The Britton-Robinson (BR) buffer solution was prepared by mixing 0.04 mol L^{-1} acetic acid, 0.04 mol L^{-1} boric acid, 0.04 mol L^{-1} phosphoric acid and 0.2 mol L^{-1} NaOH solution in a specific proportion. All chemicals used in the experiments were analytical grade without further purification and deionized water was used for the preparation of all the solutions. Formulations containing 25 mg for DS enteric-coated tablets, 50 mg for DS sustained-release tablets and 75 mg for DS sustained release capsules were purchased from local pharmacies.

2.2. Apparatus

The instruments used in this study were as follows: F-4500 spectrofluoro-photometer (Hitachi, Japan); UV-1700 spectrophotometer (Shimadzu, Japan); H-600 transmission electron microscope (Hitachi, Japan); DB-525 particle size analyzer (Brookhaven, USA); pHs-3C digital pH meter (Shanghai Lei Ci Device Works, China) with a glass electrode (Model E-201-C); Magnetic stirrer (Gongyi Yuhua Instrument Factory, China).

2.3. Preparation of AgNPs Dispersion

AgNPs were synthesized by citrate reduction of $AgNO_3$. The AgNPs dispersion (1.0×10^{-3} mol L^{-1}) was prepared as follows: 50 mL solution of $AgNO_3$ with concentration of 1.0×10^{-3} mol L^{-1} was prepared. The solution was stirred and 2.0 mL sodium citrate (1%) was added, and then the mixture solution was continued to heat at 90 °Cfor 30 min with vigorous stirring, the color of this solution changed gradually from colorless to a deep yellow and it was finally diluted to 50 mL. The synthesized AgNPs dispersion were stored at 4 °C.

2.4. Preparation of Samples

The sugar coating was carefully removed from 10 tablets and the contents were carefully pulverized. The powders were then thoroughly mixed. A portion of the mixed powder was accurately weighed and placed in a 100 mL volumetric flask. The powder was dissolved by addition of deionized water up to the mark and sonication for 10 min, and the solution was then filtered. The first 30 mL of the filtrate were discarded, a portion of the remaining filtered sample solution was diluted to the mark in a 100 mL volumetric flask, and this solution was analyzed according to the general procedure.

Urine samples were obtained from healthy volunteers before and after the ingestion of a commercial tablet containing the standard doses of DS. It should be emphasized that volunteers provided their consent after appropriate information about the study and ethical guidelines were accomplished during the complete study. Urine samples were filtered by 0.45 μm organic membrane then stored in 50 mL polyethylene bottles.

2.5. General Procedure

0.5 mL of 1.0×10^{-3} mol L^{-1} AgNPs dispersion, 1.0 mL of BR buffer solution (pH = 4.0) and certain amount of DS were added into 25 mL volumetric flask. The resulting solutions were diluted to the mark and were incubated for 5 min. The RLS spectra of the solutions were recorded by synchronously scanning the excitation and emission monochromators ($\Delta\lambda = 0$ nm) from 300 to 700 nm. Slit widths of excitation and emission were kept at 5 nm. The RLS intensity of the solution was measured at the maximum wavelength of 455 nm. The decreased RLS intensities of the solutions were calculated by the following equation: $\Delta I_{RLS} = I^0_{RLS} - I_{RLS}$ (in which I^0_{RLS} and I_{RLS} were the RLS intensities of the AgNPs in the absence and presence of DS). All the experiments were carried out at room temperature and repeated at least three times.

3. Results and Discussion

3.1. Absorption Spectra

The absorption spectra of AgNPs and AgNPs-DS solutions were displayed in Fig. 1. The absorption peak at 275 nm was observed for DS, and AgNPs had only one surface plasmon resonance absorption peak at 406 nm. However, the absorbance of the AgNPs-DS solutions linearly decreased at 406 nm with the addition of DS, and the maximal absorption peak of AgNPs did not shifted. The absorption value at 275 nm increased linearly with the increasing of DS concentration. Thus, the two systems can be used to detect DS, too. But the sensitivity is low.

3.2. RLS Spectra

When a visible light irradiated the surface of the AgNPs, the light with the same wavelength as the resonant wavelength was absorbed that induced the surface electronic collective resonance to scatter photon outward. In the present study, the RLS spectra of DS, AgNPs and AgNPs-DS were examined, and the results were displayed in Fig. 2. The RLS intensity of DS was relatively weak in the wavelength range of 300–700 nm. However, The RLS intensity of AgNPs was very strong and the maximum peak was at 455 nm. As shown in Fig. 2, with the addition of DS to AgNPs, the RLS intensities of AgNPs-DS solutions were decreased linearly at 455 nm. Therefore, the concentration of DS could be determined by RLS technique using AgNPs as probe.

3.3. Characteristics of AgNPs and AgNPs-DS

The structural characteristics such as shape and size of AgNPs and AgNPs–DS were investigated by TEM and size distribution analysis, the results were displayed in Fig. 3. As can be seen, the average diameter of the synthesized AgNPs was about 40.2 nm, the particles were comparatively homogenous, well dispersed, and without any obvious aggregation (Fig. 3A and C). The shape of the new particles of AgNPs–DS was different from that of the AgNPs and they were aggregated together and formed an inhomogeneous cluster which was obviously bigger than the original AgNPs (Fig. 3B and D). The average diameter of AgNPs-DS was about 80.7 nm.

3.4. Effect of pH

The pH of the solution played a very important role in the interaction between AgNPs and DS. Therefore, the influence of pH on ΔI_{RLS} was investigated over a pH range of 2.0–11.0, and the results were shown in Fig. 4. It can be seen that ΔI_{RLS} kept nearly constant between 3.0 and 6.0. When the pH was higher than 6.0, ΔI_{RLS} decreased remarkably with the increase of pH value. Therefore, pH 4.0 of BR buffer solution was chosen for further research.

3.5. Effect of Reaction Time and Temperature

The effects of reaction time and temperature were tested by equilibrating 0.5 μg mL^{-1} DS and AgNPs 2.0×10^{-5} mol L^{-1} at pH 4.0 under different reaction times and temperatures, respectively. As shown in Fig. 5, the ΔI_{RLS} reached maximum at 5 min and remained stable for over 2 h. The optimum temperature range was found to be 10–30 °C. When the temperature was higher than 30 °C, the ΔI_{RLS} decreased due to the increase in thermal motion of the particles resulting