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Silver nanoparticles enhanced flow injection chemiluminescence determination of gatifloxacin in pharmaceutical formulation and spiked urine sample

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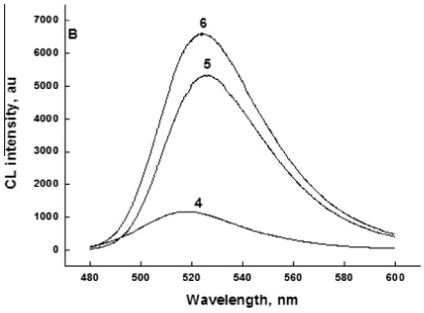
HIGHLIGHTS

- Precise and reliable method was developed for the determination of gatifloxacin.
- Silver nanoparticle was used as chemiluminescence enhancer.
- This method is easily performed and affords good precision and accuracy.
- The sensitivity of this technique does not affected by coexisting ions/compounds.
- The method was successfully applied to analysis of drug and spiked urine.

GRAPHICAL ABSTRACT

CL spectra for the quantitative analysis of GFLX; (4) calcein–$KMnO_4$ system, (5) calcein–$KMnO_4$–GFLX system and (6) calcein–$KMnO_4$–GFLX–AgNP system; conditions: [GFLX] = 1.0×10^{-5} M, [calcein] = 1.0×10^{-4} M, [$KMnO_4$] = 7.0×10^{-4} M, [NaOH] = 0.05 M, [AgNP] = 5.0×10^{-4} M.



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ABSTRACT

Silver nanoparticles have been utilized for the enhanced chemiluminogenic estimation of fluoroquinolone antibiotic gatifloxacin. It has been found that the weak chemiluminescence intensity produced from the reaction between calcein and $KMnO_4$ can further be strengthened by the addition of silver nanoparticles in the presence of gatifloxacin. This phenomenon has been exploited to the quantitative determination of gatifloxacin. Under the optimum experimental conditions, the calibration curves are linear over the range of 8.9×10^{-9}–4.0×10^{-6} M, while the limits of detections were found to be 2.6×10^{-9} M with correlation coefficient value (r^2) 0.9999. The relative standard deviation calculated from six replicate measurements (1.0×10^{-4} M gatifloxacin) was 1.70%. The method was applied to pharmaceutical preparations and the results obtained were in reasonable agreement with the amount labeled on the formulations. The proposed method was also used for the determination of gatifloxacin in spiked urine samples with satisfactory results. No interference effects from some common excipients used in pharmaceutical preparations have been found.

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Introduction

Gatifloxacin (GFLX) chemically named as 1-cyclopropyl-6-fluoro-8-methoxy-7-(3-methylpiperazin-1-yl)-4-oxo-quinoline-3-carboxylic acid, is an 8-methoxy fluoroquinolones (FQs) with a 3-methylpiperazinyl substituent at C7 used as antibacterial agent with a broad spectrum of activity against Gram-positive and Gram-negative organism. It's application is effective in a range of clinical infections, including community-acquired pneumonia, acute exacerbations of chronic bronchitis, acute sinusitis and genitor urinary tract infections [1,2]. It exhibits enhanced activity against clinically relevant pathogens, including such common respiratory pathogens as *Streptococcus pneumoniae*, *Haemophilus influenzae*, *Mycoplasma pneumoniae*, *Chlamydia pneumoniae*, *Moraxella catarrhalis*, and Legionella [3]. Clinical cure rates in all trials of patients treated with GFLX were 90% or higher. Like other new FQs, GFLX has a dual mechanism of action, inhibiting both bacterial DNA gyrase and topoisomerase IV [4]. GFLX is a metabolically stable compound; >80% of the drug is excreted in the urine unchanged. Up to 72 h after administration of single-dose GFLX (400 mg), the amounts of ethylenediamine and methylethylenediamine metabolites recovered were each 0.03% of the total administered dose [5]. The extensive need for clinical and pharmacological study require fast and sensitive analytical techniques for the determination of their presence in biological and pharmaceutical preparations [6].

Several methods have been reported in the literature for determination of GFLX. Li et al. [7] developed a spectrophotometric method for the determination of GFLX. A first and second derivative spectrophotometric method and validation for the determination of GFLX in bulk and pharmaceutical dosage forms have been reported [8]. The quantitative determination of the drug was carried out using the first derivative values measured at 276 nm and the second derivative values measured at 287 nm ($n = 6$). A terbium-sensitized spectrofluorometric method using an anionic surfactant, sodium dodecyl benzenesulfonate (SDBS), was developed by Guo et al. [9] for the determination of GFLX. A coordination complex system of GFLX–Tb(III)–SDBS was studied. SDBS significantly enhanced the FL intensity of the complex. A HPLC method was developed for the assay of GFLX in tablets [10]. Motwani et al. [11] has reported a stability indicating high-performance thin-layer chromatographic method for the determination of GFLX. The method employed thin-layer chromatographic aluminum plates precoated with silica gel 60F-254 as the stationary phase and the mobile phase consisted of *n*-propanol-methanol-concentrated ammonia solution. Salgado et al. [12] developed a specific agar diffusion bioassay for the antibacterial GFLX using a strain of *Bacillus subtilis* ATCC 9372 as the test organism. Except aforementioned method, different others analytical method have also been put forward such as HPLC with diode-array and FL detection [13], thin layer chromatography [14] and chemiluminescence (CL) [15].

In this study, silver nanoparticles (AgNP) have been utilized in order to quantitative estimation of the essential fluoroquinolone antibiotics, namely, GFLX. AgNPs were prepared based on aqueous-gaseous phase reaction of silver nitrate solution and ammonia gas [16,17]. Few other methods for synthesis of AgNP were reported in the literature by reduction of silver nitrate with other drug, including ascorbic acid, [18,19], β-D-glucose [20], heparin with glucose in the presence of *n*-hexadecyltrimethylammonium bromide [21,22] and adrenaline [23]. AgNPs were found to enhance intensity of the CL reaction between calcein and $KMnO_4$. AgNP displayed a good catalysis effect, by which the CL intensity of calcein–$KMnO_4$ was strongly increased in the presence of GFLX. Based on this phenomenon, a flow-injection CL assay was developed to detect GFLX in pharmaceutical formulations and biological samples.

Chemicals and sample preparations

Chemicals and reagent

All chemicals were of analytical reagent grade and were used without further purification. Distilled deionized (DI) water (Millipore, MilliQ Water System, USA) was used throughout. GFLX were purchased from Sigma–Aldrich (St. Louis, USA). Stock solutions (1.0×10^{-3} M) of GFLX was prepared in deionized water. Working solutions of desired concentrations were freshly prepared by appropriate dilution of each stock solution with DI water. Calcein was purchased from Sigma Corporation (Steinheim, Germany). The 1.0×10^{-4} M working solution of calcein was prepared by dissolving 0.0310 g of calcein and then diluting to 500 ml with DI water silver nitrate and ammonia solution were purchased from Sigma (Louis, USA).

Sample preparations

Pharmaceutical drug

Sample solutions for analysis were prepared as follows. The average tablet weights were calculated from the weight of each of 10 tablets which were selected from the same group randomly. An accurately weighed portion of each homogenized sample containing 400 mg of GFLX (Gatizen) (Ulticare, Alkem Laboratories Ltd, Mumbai, India) was transferred into 1000 ml calibrated dark flask containing 500 ml of water and dissolved in ultrasonic bath for 20 min and diluted with DI water to mark. The dissolved sample was filtered through Millipore membrane filter paper (MF-Millipore™, 0.8 μm pore size and 150 μm thickness, USA) and diluted with water to volume to obtain the appropriate concentration for analysis.

Urine sample collection

Blank urine samples were kindly provided by several volunteers of ages between 25 and 45 years. Immediately after collection, 25 ml aliquots of urine samples from 5 volunteers were spiked with GFLX at variable concentration levels, in order to calculate the recoveries of the proposed method. From these pools, each 0.5 ml aliquots were distributed to 0.5 ml Eppendorf and stored at −18 °C until analysis.

Preparation of NP

AgNP were prepared as follows with modifications [24]. The synthesis was based on the aqueous–gaseous phase reaction of silver nitrate solution and ammonia gas [16]. To a 100 ml two neck round bottom flask 50 ml of silver nitrate solution (1.0×10^{-3} M) was added and the flask was placed into a constant temperature oil bath on a magnetic stirrer. 50 ml ammonia solution (1 M) was added to another 500 ml flask kept in a water bath at room temperature. The flasks were connected with glass tubes through which ammonia gas volatilized and diffused slowly into the flask of silver nitrate. Ammonia solution then reacted with silver nitrate. The whole system was exposed to the light of daylight lamp. AgNP were prepared in the five steps: (1) silver nitrate containing flask was kept under stirring (~70 °C oil bath) for 6 h, (2) settling the flask for 6 h without stirring and heating, (3) following step 1 for 5 h, (4) repeating the step 2 and (5) following step 1 for 3 h.

Analytical procedure

The flow injection analysis (FIA) configuration consisted of a three-channel manifold using two pumps. For calcein based CL system, prior to the CL measurement acquisition, calcein stream was