Bioprocess Biosyst Eng (2015) 38:1803–1810
DOI 10.1007/s00449-015-1433-4

ORIGINAL PAPER

Flow-injection chemiluminescence method for the determination of moxifloxacin in pharmaceutical tablets and human urine using silver nanoparticles sensitized calcein–$KMnO_4$ system

Saikh Mohammad Wabaidur[1] · Seikh Mafiz Alam[2] · Zeid A. Alothman[1] · Masoom Raza Siddiqui[1] · Mu Naushad[1] · Ayoub A. Alqadami[1]

Received: 27 January 2015 / Accepted: 24 May 2015 / Published online: 24 June 2015

Abstract Silver nanoparticles have been synthesized and were utilized for the enhanced luminometric estimation of moxifloxacin antibiotic. During the experimental procedure, it was clearly found that the addition of silver nanoparticles intensifies the weak chemiluminescence signal intensity of calcein–$KMnO_4$ system by several folds. It was also obvious that the intensity enhancement was linearly proportional to the moxifloxacin concentration and this phenomenon was further utilized for the quantitative determination of target analyte. Effects of the different chemical variables during the experiment were studied to achieve best chemiluminescence signal. Under the optimized experimental parameters, the linear calibration graph was established over the moxifloxacin concentration range of 6.0×10^{-8} M to 2.5×10^{-6} M with coefficient of correlation (r^2) value 0.9998. The lower detection limit was found to be 5.6×10^{-9} M. The percentage relative standard deviation calculated from five replicate chemiluminescence measurements was found to be 2.63 %. The developed chemiluminescence technique was successfully applied to the determination of moxifloxacin in tablet formulation and spiked human urine sample.

✉ Saikh Mohammad Wabaidur
tarabai22@yahoo.com.sg

✉ Seikh Mafiz Alam
mafizchem@gmail.com

[1] Advanced Materials Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia

[2] Department of Chemistry, Aliah University, Kolkata, West Bengal, India

Keywords Silver nanoparticles · Moxifloxacin · Calcein · Chemiluminescence · Flow-injection analysis

Introduction

Moxifloxacin (MF) chemically known as (1-cyclopropyl-7-[2,8-diazobicyclo(4.3.0)nonane]-6-fluoro-8-methoxy-1,4-dihydro-4-oxo-3-quinolone carboxylic acid), generally is a new 8-methoxyquinolone derivative of fluoroquinolone (FQ) that possesses enhanced in vitro activity against Gram-positive bacteria and maintained its activity against Gram-negative bacteria [1–3]. It has been used as chemotherapeutic bactericidal drug and belongs to the third-generation FQs family [4]. Also the efficiency of oral MF 400 mg (once per day) has been well reported in the recovery of acute sinusitis caused by bacteria and simple skin and skin structure infections. The bactericidal activity of this analyzed antibiotic is facilitated by the reticence of DNA gyrase including topoisomerase II and topoisomerase IV which are normally the crucial enzymes responsible for bacterial DNA replication, recombination, repair and transcription [5]. MF dose is generally provided to patients in the amount of 400 mg per day, and consequently the final amount of the drug can be found in urine and serum for the treated patients are of 30.00–60.00 μg/ml and 2.00–5.00, respectively [6]. Thus, considering the clinical benefits of MF, there has been a large increase in the production of MF formulations in market in recent past. Therefore, due to its vast clinical applications it is of high demand to establish a reliable, simple and sensitive procedure for the quantitation of MF drug.

Many methodologies have been reported in the literature by researchers in the last few decades. Most of the developed methodologies for the determination of MF are

mainly based on conventional or hyphenated liquid chromatography including high-performance liquid chromatography–fluorescence detection (HPLC–FL) [7], solid phase extraction coupled with HPLC [8], liquid chromatography–electrospray ionization mass spectrometry [2] and direct HPLC [9]. On the other hand, Motwani et al. [10] established and validated a spectrophotometric technique for the estimation of MF in bulk and pharmaceutical tablet formulations. Differential pulse polarographic [11] and electroanalytical detection [12, 13] methods were also reported in the literature to quantify the trace amount of MF in pharmaceutics, serum and urine samples. The viability of capillary electrophoresis coupled with He–Cd laser-induced FL detection was described for the determination of MF [14], while Ocana et al. [15] established a spectrofluorimetric method to determine MF in pharmaceuticals, human serum and urine samples.

In recent years, nanoparticle (NP) of metals has been investigated extensively in many research fields. Among them, silver nanoparticle (AgNP) has been extensively studied due to their beneficial catalytic, electrical, optical and properties [16–18]. With the vast progress of awareness in the field of nanotechnologies and the spectral theories, the luminescence properties of metal NP have also been testified [19–22]. Although several methods have been reported for moxifloxacin determination, yet there is no method reported using the silver nanoparticles as fluorescence enhancer. The method includes low-cost instrumentation as compared to the HPLC and LC–MS involving the solid phase extraction. Although the electrochemical methods are more sensitive, they need tedious electrode cleaning steps. The reported CL method is simple, sensitive, rapid, reproducible, and involves easy sample preparation that does not require tedious extraction processes. Therefore, in the proposed study a simple and highly sensitive chemiluminescence (CL) technique has been developed, where the weak signal of calcein–$KMnO_4$ CL system was enhanced by introducing AgNP in the presence of MF. Based on this occurrence, a new flow-injection CL method was developed to determine MF contents in pharmaceutical formulations and biological samples, namely human urine.

Experimental section

Chemicals

All the reagents were of analytical grade and were used without further refinement. Distilled deionized (DI) water (Millpore, MilliQ Water System, USA) was utilized throughout. Moxifloxacin standard was supplied by Sigma-Aldrich (St. Louis, USA). Stock standard solutions (1.0×10^{-3} M) of MF were prepared in DI water. All the experimental solutions were newly prepared before carrying out the analysis by proper dilution with DI water. Calcein was obtained from Sigma Corporation (St. Louis, USA). The calcein solution of 1.0×10^{-4} M was made by dissolving 0.0310 g of calcein and in 500 ml DI water. Both ammonia solution and silver nitrate standard were bought from Sigma (St. Louis, USA).

Apparatus

The schematic illustration of the proposed flow-injection analysis (FIA) system is shown in Fig. 1. Briefly, two peristaltic pumps (Model 404, Ismatec, Zurich, Switzerland) were employed to carry all the working solutions. Pump P_1 delivered AgNP solution which was combined with analyte solution in a Rheodyne (Model 7125, Cotati, CA, USA) six-way injection valve through a loop. On the other hand, pump P_2 was responsible for transferring all other CL reagents, while the flow rate for each line was kept equal. Polytetrafluoroethylene (PTFE) tubing (0.8 mm i.d.) was employed throughout the FIA manifold to convey all analysis solutions into the absorbance cell. A Spex (Model F111, SPEX industries, Edison, NJ, USA) spectrofluorimeter furnished with a coiled glass flow cell (1.0 mm i.d., 20 mm total diameter) was utilized for

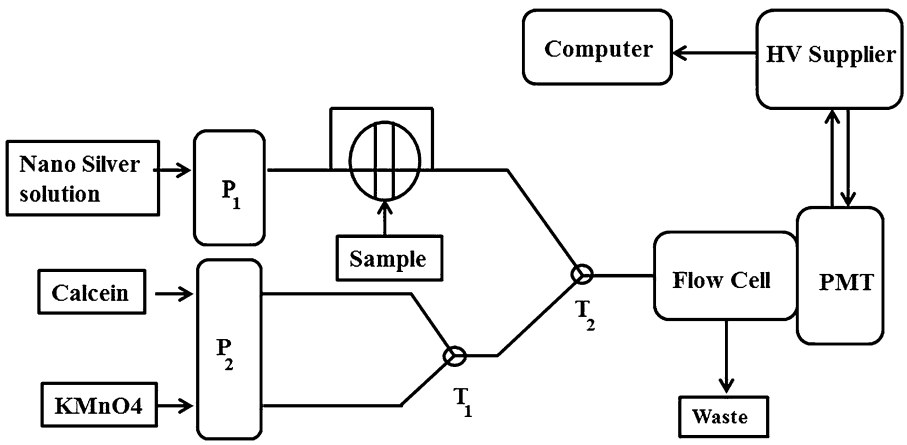

Fig. 1 Schematic of the FIA CL manifold. P_1, P_2 peristaltic pumps, T_1, T_2 Y-pieces

identifying and recording the CL intensity of the reaction yield. Data collection and data analysis were achieved by the Spex DM 3000 program. During the CL measurement, the light source of the spectrofluorimeter was kept switched off, while the emission monochromator slit width was 0.25 mm and the high voltage for the photomultiplier tube (Model R 928, Hamamatsu, Japan) was set at 950 V.

Pharmaceutical sample preparations

The average weights of ten tablets randomly selected from the same group were calculated. Then a required portion of each homogenized sample containing 400 mg of MF (Avolex) was shifted into 1000-ml Erlenmeyer dark flask having 500 ml of water followed by sonication in ultrasonic bath for 20 min and further diluted with DI water up to the label mark. Finally, the prepared MF sample was filtered using Millipore membrane filter paper and diluted in DI water to volume to obtain the required concentration of the analytes for analysis.

Urine sample gathering

Blank urine samples from healthy volunteers of ages around 30–40 years were collected. Instantaneously after collection of urine, 25-ml aliquots of samples from five volunteers were spiked with MF separately at various concentration levels. This was performed to determine the recoveries of the proposed CL method. After that the 0.5 ml aliquots from each pool were spread to 0.5 ml Eppendorf and stored at −18 °C inside the refrigerator until analysis.

Preparation of AgNPs

Silver nanoparticles were prepared as our previously reported methods, which was adopted from reported literature with some modifications [23]. The synthesis of NPs was mainly based on the aqueous and gaseous phase reaction between the $AgNO_3$ solution and the NH_3 gas. At the starting of the preparation process, 50 ml of silver nitrate solution of 1.0×10^{-3} M was taken into a 500-ml two-neck round-bottomed flask and the flask was positioned into a oil bath on a magnetic stirrer by keeping the temperature constant. After that, 1 M ammonia solution of volume 60 ml was added to another 500-ml conical flask and kept in a water bath at room temperature. Both flasks were connected using glass tubes through which volatilized ammonia gas passes and then diffused slowly into the flask containing $AgNO_3$ and the reaction between them start to occur. The whole experimental setup was exposed to the light of daylight lamp to supply heat. In brief, the main steps involved during AgNPs preparations can be summarized as follows: firstly, $AgNO_3$ solution containing flask was kept under stirring (~75 °C oil bath) for 6 h; secondly, the flask was allowed to settling for another 6–7 h without any stirring as well as heating; thirdly, the step one was followed for another 4–5 h; In the fourth step, the step 2 was repeated; and finally the step 1 was performed for 3½ h in the fifth step.

Analytical procedures

The used FIA configuration of the current study consisted of a three-channel manifolds that using two pumps P_1 and P_2. In the proposed calcein–$KMnO_4$ flow-injection CL system, the pump P_2 delivers calcein and $KMnO_4$ solution which are mixed in the three-way "T_1" connector of the FIA system. On the other hand, the pump P_1 delivers the AgNP solution, which is then mixed with the solution containing the target compound through the injection valve. Both the streams were then combined in the second "T_2" connector and after that enter into the flow cell in the fluorimeter, accompanying with the increase of the CL intensity. The enhancement in the CL intensity was noticed once the AgNP solution was introduced into the carrier stream of the FIA. The obtained CL signals corresponding to a blank was found to be proportional to the sample concentration and hence was used as analytical signal for the quantitative analysis purpose of MF. The comprehensive FlA system used during the experiment is schematically presented in Fig. 1.

Results and discussion

Transmission electron microscopy image and UV spectral characteristics

Transmission electron microscopy (TEM) image of AgNP showed that the average particle size is about 14 nm and the dispersions of NPs are good (Fig. 2a). The desired size of AgNPs was controlled by keeping the concentration of ammonia gas very low and maintained throughout the synthesis process [23]. The scattering component of metal nanoparticles is responsible for luminescence enhancement and the scattering component depends on the size and shape of the nanoparticles. And since the chemiluminescence is an energy transfer process so the distance between the nanoparticles and fluorophore also plays an important role. Also the absorption maxima of the silver nanoparticles changes inside the visible region on the basis of their size. In chemiluminescence the spectral overlap for the resonance energy transfer of the metal nanoparticle with spectrum (excitation/emission) of the fluorophore is also very important [24]. Therefore, the size controllability and

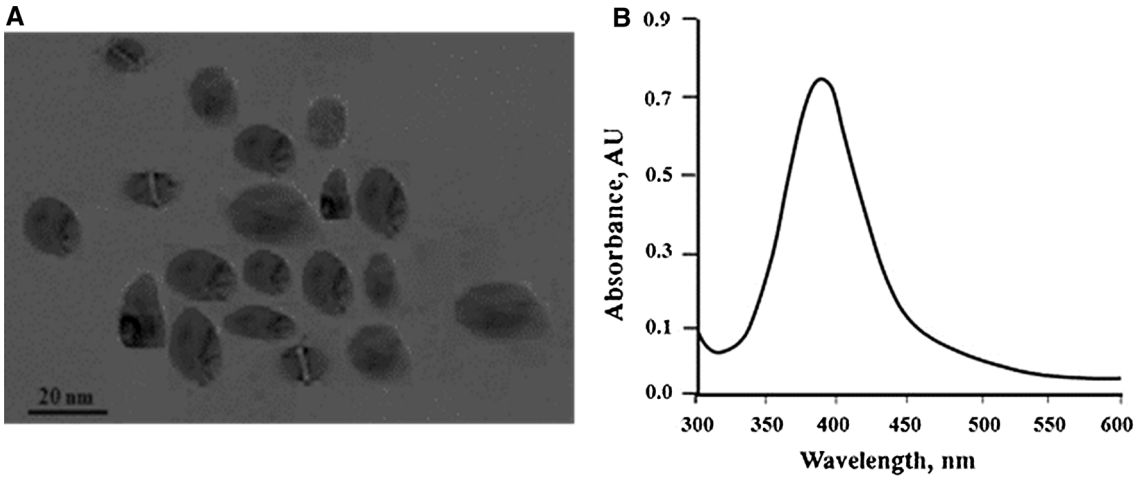

Fig. 2 TEM image (**a**) and UV-vis absorption spectra (**b**) of the synthesized AgNP

tunability for the preparation of the nanoparticles are very important as it can produce monodisperse AgNPs with a desired shape and size which are responsible for luminescence enhancement of the proposed system [25]. The UV–Vis spectrum of the synthesized AgNP showed (Fig. 2b) an absorption peak near 390 nm, which is the characteristic absorbance wavelength of silver [26]. The narrow peak of the UV-absorption spectrum confirmed the higher monodispersity level of the synthesized AgNP in the solution [27–29].

CL parameters optimizations

Oxidizing agent selection

The effects of different oxidizing agents on CL intensity of the proposed CL method were investigated. Oxidizing agents including $KMnO_4$, $K_3Fe(CN)_6$, KIO_3, $Ce(SO_4)_2$, $KBrO_3$ were tested. 1.0×10^{-4} M solutions of $KMnO_4$, $Ce(SO_4)_2$, $KBrO_3$ and KIO_3 were prepared in 1.0×10^{-2} M H_2SO_4 while the $K_3Fe(CN)_6$ was made in 0.1 M NaOH. The experimental results showed that the CL intensity was strongly dependent on oxidizing agents. Among the tested oxidizing agents, the utmost CL intensity was achieved when $KMnO_4$ was utilized and was chosen for further experimentation.

Optimization of calcein concentration

The effect of calcein concentration on CL intensity was investigated during the chemiluminogenic determination of MF. The calcein concentration was tested over the concentration range from 1.0×10^{-6} M to 1.0×10^{-3} M in triplicate and the standard deviation was found in the range of 0.028–0.143, while the concentration of MF was kept at 1.0×10^{-4} M. The results obtained are shown in Fig. 3. It

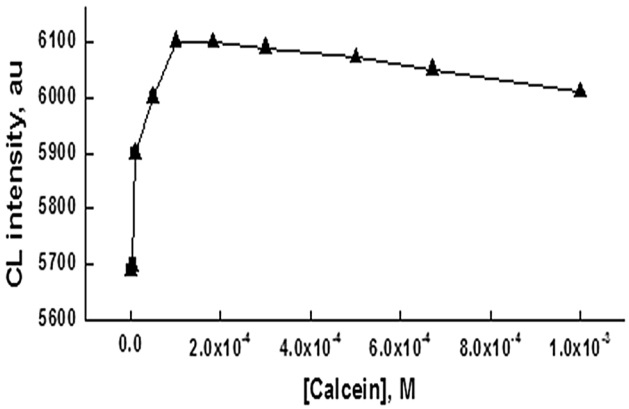

Fig. 3 Effect of calcein concentration on the CL intensity for the determination of MF

was clearly seen that the CL intensity is strongly dependent on calcein concentration. Up to the calcein concentration 1.0×10^{-4} M, the CL intensity increased and then become nearly constant. Hence, 1.0×10^{-4} M calcein was chosen as optimum concentration for the determination of MF. The higher CL reaction rate of calcein might be responsible for increasing CL intensity with increasing calcein concentration.

Selection of $KMnO_4$ concentration

To acquire the optimum concentration of $KMnO_4$ which was used for the chemiluminogenic reaction for the quantitation of MF, the influence of $KMnO_4$ concentration on the CL intensity was examined. $KMnO_4$ was employed in the proposed CL system as the oxidant. Therefore, the concentration of $KMnO_4$ could affect the CL signal intensity of the systems. The $KMnO_4$ concentration was tested in the range of 1.0×10^{-6} M to 1.0×10^{-3} M in triplicate under the fixed amount of calcein (1.0×10^{-4} M) and MF (1.0×10^{-4} M) (Fig. 4). The

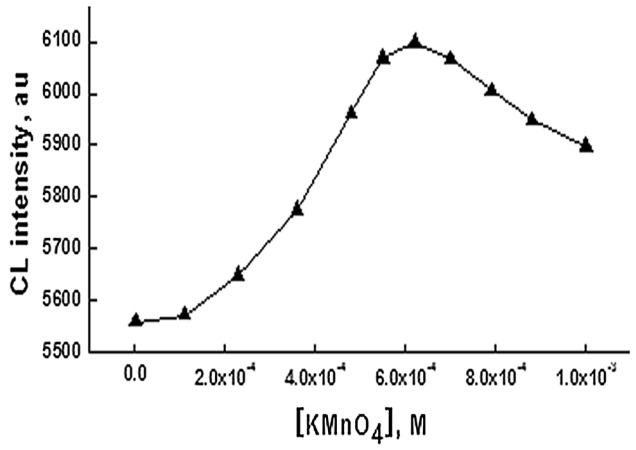

Fig. 4 Dependence of $KMnO_4$ on the CL intensity for the determination of MF

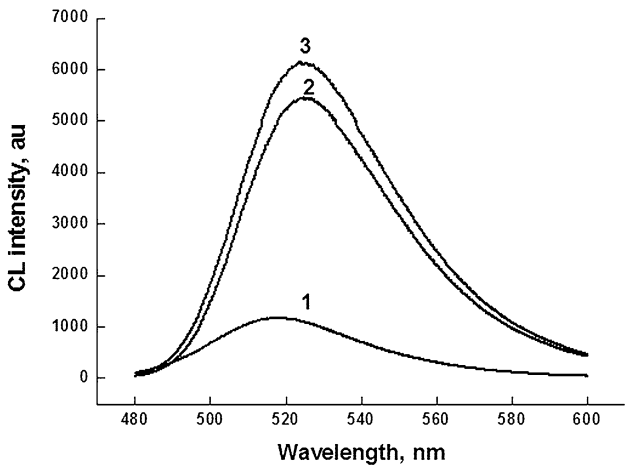

Fig. 5 **a** CL spectra for the quantitative analysis of MF; *1* calcein–$KMnO_4$ system, *2* calcein–$KMnO_4$–MF system and *3* calcein–$KMnO_4$–MF–AgNP system; conditions: [MF] = 1.0×10^{-5} M, [calcein] = 1.0×10^{-4} M, [$KMnO_4$] = 6.1×10^{-4} M, [NaOH] = 0.05 M, [AgNP] = 5.0×10^{-4} M

experimental results indicate that the CL intensity increased up to 6.1×10^{-4} M and then started to decrease gradually. Hence 6.1×10^{-4} M $KMnO_4$ was chosen as optimum. The standard deviation for the optimization of $KMnO_4$ was found to be 0.167–0.243.

NaOH concentration

The calcein–$KMnO_4$ CL reaction was accomplished in alkaline medium. To adjust the alkalinity of reaction medium the concentration of NaOH in potassium permanganate solution was varied under the discrete concentration of MF (1.0×10^{-4} M). The influence of NaOH concentration on the CL reaction was analyzed in the range 1.0×10^{-3} M to 1.0 M by keeping other parameters constant. The highest CL intensity for the proposed system was observed at 0.05 M concentration of NaOH. Hence 0.05 M was chosen as optimum NaOH concentration for future experiment.

Flow rate

The flow rate of reagent solutions played an important role in CL measurements, as the time consumed to transfer the excited product into the flow cell is critical parameter for achieving maximum amount of the emitted light [30]. Therefore, the effect of flow rate was studied over the range 1.0–4.5 ml/min with equal flows in each channel, while keeping all other conditions as constant. The result showed that once the flow reached 2.0 ml/min the maximum CL intensity was observed, which might due to the decreasing dispersion [31]. On further increasing the flow rate, no significant change in the analytical signal was observed. It was observed that with a higher flow rate consumption of reagent increased and both the measurement rate and the peak shape were affected simultaneously due to lower residence time (<30 s) [31]. Hence, a flow rate of 2.0 ml/min in each channel was selected as optimum flow.

AgNP concentration

The significance of AgNP concentration on the proposed CL reaction of calcein–$KMnO_4$ was investigated over the concentration range of 1.0×10^{-4} M to 1.0×10^{-3} M, while the concentration of other experimental parameters including, MF, calcein and $KMnO_4$ were kept fixed at 1.0×10^{-4} M, 1.0×10^{-4} M and 6.1×10^{-4} M, respectively. The obtained results showed that the appropriate concentration of AgNPs to attain the best CL intensity signal was 5.0×10^{-4} M. Further increase in the AgNPs concentration results in decrease of the CL intensity of the system that might be attributed due to the strong interaction among the particles and the CL energy transferred among particles which are in small distance.

CL spectra of the systems

The CL intensity of proposed calcein–$KMnO_4$ system in the absence and in the presence of MF drug was recorded with the emission monochromator, respectively. The obtained experimental results indicated that an ultra-weak CL signal of calcein–$KMnO_4$ reaction system was largely enhanced and the increased intensity is proportional to the concentration of the substance added. The addition of AgNP into the reaction system leads to further increment in the CL by several folds (Fig. 5).

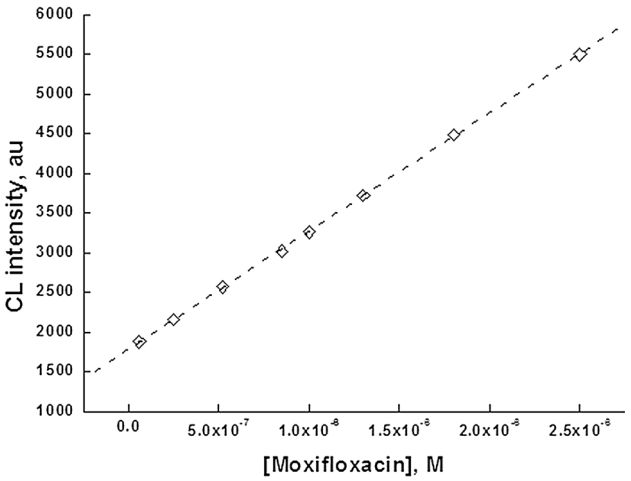

Fig. 6 Calibration curves for MF obtained by the AgNP enhanced calcein–$KMnO_4$ CL system

Analytical features

The calibration curve for target analyte was constructed using a set of eight standard solutions of MF under the optimized experimental parameters conditions, such as, concentration of calcein, $KMnO_4$, NaOH and AgNP was 1.0×10^{-4} M, 6.2×10^{-4} M, 0.05 M and 5.0×10^{-4} M, respectively. The results confirm that the concentration of MF is linear over a MF concentration range of 6.0×10^{-8} M to 2.5×10^{-6} M ($r^2 = 0.9998$) (Fig. 6). The lower limit of detection for the proposed method was found to be 5.0×10^{-9} M and relative standard deviation (RSD) ($n = 5$) for 1.0×10^{-4} M of MF is 2.63 %.

Table 1 Maximum tolerable concentration ratios of interferents and MF (1.0×10^{-5} M) in the proposed CL system

Interference species		Interference species: MF
Ions	Biological compounds	
Na^+, K^+		100
Al^{3+}, Ca^{2+}, Mg^{2+}		90
	Starch, fructose, glucose	50
	Sucrose, dextrin, lactose, galactose	45
	Aspirin	20

Interference study

The interference of some ions and biological compounds including, Na^+, K^+, Al^{3+}, Ca^{2+}, Mg^{2+}, starch, fructose, glucose, sucrose, dextrin, lactose, galactose and aspirin those might be present in the tablet formulation was studied. For this purpose, addition of increasing concentrations of these interference compounds to 1.0×10^{-5} M MF solution was performed until more than 5 % variation in CL intensity was achieved. The results present in Table 1 shows that most of the interferents were found to have no significant interference effect for the quantitative determination of target compound.

Real sample analysis

The validation of the proposed CL method was established by analyzing the commercial pharmaceutical formulations, namely Avolex (containing 400 mg of MF). Firstly, the total contents of 10 tablets are finely ground tablets were weighed and mixed to make them homogeneous. Then, an equivalent of one tablet amount was weighed and dissolved in DI water with continuous shaking for 20 min using an ultrasonic bath. Then the final solution was filtered using Millipore membrane filter, and the filtrates were diluted accordingly to meet the linear range. The results presented in Table 2 shows that the overall recovery was about 96.0–96.5 %. Thus, it could be concluded that, there were no notable changes between the labeled contents and the amount obtained by the proposed method. The proposed method was then applied to the determination of targeted antibiotic in spiked human urine samples (Table 3). The percentage recovery of the analyzed drug was found to be between 95.5 and 97.2 %. The results indicate that the proposed CL procedure is simple, sufficiently sensitive and selective for the determination of analyzed compound in urine sample.

Conclusions

This preliminary study shows that MF exhibits analytically useful CL upon reaction with calcein–$KMnO_4$ system. The application of silver nanoparticles showed great influence in enhancing the weak CL intensity of the proposed

Table 2 Analysis of MF in pharmaceutical formulations by proposed AgNP enhanced calcein–$KMnO_4$ CL system and recovery studies

Sample	Label claimed	Found ± RSD[a]	Added ($\times 10^{-7}$ M)	Found ($\times 10^{-7}$ M)	Recovery mean ± RSD[a] (%)
Avolex	400 mg of MF	389.1 ± 0.17	2.5	2.47	96.0 ± 1.4
			4.5	3.86	96.5 ± 0.5
			6.5	6.35	97.7 ± 1.5

[a] Mean of three measurements

Table 3 Analysis of MF in spiked human urine samples by AgNP enhanced calcein–$KMnO_4$ CL system

Sample	Added ($\times 10^{-7}$ M)	Found ($\times 10^{-7}$ M)	Recovery (%) Mean ± RSD[a]
MF	2.00	1.93	96.5 ± 0.5
	4.00	3.92	98.0 ± 1.6
	6.00	5.82	97.0 ± 0.7

[a] Mean of three measurements

calcein–$KMnO_4$ CL system. However, the obtained calcein–$KMnO_4$ CL signal was further strengthened due to the addition of AgNP in the presence of MF. This enhancing phenomenon was adapted to the quantitative determination of target analyte in commercial pharmaceutical drug formulation and spiked human urine. The linearity of the calibration curves was found over the range of 6.0×10^{-8} M to 2.5×10^{-6} M ($r^2 = 0.9998$). The limit of detection was found to be 5.6×10^{-9} M, while the RSD calculated from five replicate measurements was 2.63 %. The developed CL method was effectively applied to the quantitation of MF in pharmaceutical tablet formulations and urine samples. There were no significant interference effects observed from some common excipients usually added during the preparations of pharmaceutical drugs.

Acknowledgments The authors would like to extend their gratitude to the Deanship of Scientific Research, College of Science Research Center, King Saud University, Riyadh, Saudi Arabia for supporting this project.

References

1. Donati M, Rodriguez Fermepin M, Olmo A, D'Apote L, Cevenini R (1999) Comparative in vitro activity of moxifloxacin, minocycline and azithromycin against *Chlamydia* spp. J Antimicrob Chemother 43:825–827
2. Vishwanathan K, Bartlett MG, Stewart JT (2002) Determination of moxifloxacin in human plasma by liquid chromatography electrospray ionization tandem mass spectrometry. J Pharm Biomed Anal 30:961–968
3. Biedenbach DJ, Barrett MS, Croco MAT, Jones RN (1998) Diagn Microbiol Infect Dis 32:307–311
4. Ball P (2000) Quinolone generations: natural history or natural selection. J Antimicrob Chemother 46:17–24
5. Pestova E, Noskin GA (2000) Intracellular targets of moxifloxacin: a comparison with other fluoroquinolones. J Antimicrob Chemother 45:583–590
6. Wise R, Andrews JM, Marshall G, Hartman G (1999) Pharmacokinetics and inflammatory-fluid penetration of moxifloxacin following oral or intravenous administration. Antimicrob Agents Chemother 43:1508–1510
7. Kumar AKH, Ramachandran G (2009) Simple and rapid liquid chromatography method for determination of moxifloxacin in plasma. J Chromatogr B 877:1205–1208
8. Raju B, Ramesh M, Borkar RM, Srinivas R, Padiya R, Banerjee SK (2012) In vivo metabolic investigation of moxifloxacin using liquid chromatography/electrospray ionization tandem mass spectrometry in combination with online hydrogen/deuterium exchange experiments. Rapid Commun Mass Spectrom 26:1817–1831
9. Djurdjevic AL, Stankov MJ, Djurdjevic P (2006) Optimization and validation of the direct HPLC method for the determination of moxifloxacin in plasma. J Chromatogr B 844:104–111
10. Motwani SK, Chopra S, Ahmad FJ, Khar RK (2007) Validated spectrophotometric methods for the estimation of moxifloxacin in bulk and pharmaceutical formulations. Spectrochim Acta A 68:250–256
11. İnam R, Mercan H, Yılmaz E, Uslu B (2007) Differential pulse polarographic determination of moxifloxacin hydrochloride in pharmaceuticals and biological fluids. Anal Lett 40:529–546
12. Trindade MAG, da Silva GM, Ferreira VS (2005) Determination of moxifloxacin in tablets and human urine by square-wave adsorptive voltammetry. Microchem J 81:209–216
13. Erk N (2004) Voltammetric behaviour and determination of moxifloxacin in pharmaceutical products and human plasma. Anal Bioanal Chem 378:1351–1356
14. Moller JG, Stass H, Heinig R, Blaschke G (1998) Capillary electrophoresis with laser induced fluorescence: a routine method to determine moxifloxacin in human body fluids in very small sample volumes. J Chromatogr B 716:325–334
15. Ocana JA, Callejon M, Barragán FJ (2000) Terbium-sensitized luminescence determination of levofloxacin in tablets and human urine and serum. Analyst 125:1851–1854
16. Henglein A, Meisel D (1998) Spectrophotometric observations of the adsorption of organosulfur compounds on colloidal silver nanoparticles. J Phys Chem B 102:8364–8366
17. Li W, Guo Y, McGill K, Zhang P (2010) A facile synthesis of Ag nanoparticles for mercury ion detection with high sensitivity and selectivity. New J Chem 34:1148–1152
18. Mallick K, Witcomb M, Scurrell M (2006) Silver nanoparticle catalysed redox reaction: an electron relay effect. Mater Chem Phys 97:283–287
19. Wang CC, Luconi MO, Masi AN, Fernández LP (2009) Derivatized silver nanoparticles as sensor for ultra-trace nitrate determination based on light scattering phenomenon. Talanta 77:1238–1243
20. Jin R, Cao YW, Mirkin CA, Kelly KL, Schatz GC, Zheng JG (2001) Photoinduced conversion of silver nanospheres to nanoprisms. Science 294:1901–1903
21. Kottmann JP, Martin OJF, Smith DR, Schultz S (2000) Spectral response of plasmon resonant nanoparticles with a non-regular shape. Opt Exp 6:213–219
22. Kottmann JP, Martin OJF (2001) Influence of the cross section and the permittivity on the plasmon-resonance spectrum of silver nanowires. Appl Phys B 73:299–304
23. Liu C, Yang X, Yuan H, Zhou Z, Xiao D (2007) Preparation of silver nanoparticle and its application to the determination of ct-DNA. Sensors 7:708–718
24. Chen Y, Munechika K, Ginger DS (2007) Dependence of fluorescence intensity on the spectral overlap between fluorophores and plasmon resonant single silver nanoparticles. Nanoletters 7:690–696
25. Pietrobon B, McEachran M, Kitaev V (2009) Synthesis of size-controlled faceted pentagonal silver nanorods with tunable plasmonic properties and self-assembly of these nanorods. ACS Nano 3:21–26
26. Park HW, Alam SM, Lee SH, Karim MM, Wabaidur SM, Kang M, Choi JH (2009) Optical ascorbic acid sensor based on the fluorescence quenching of silver nanoparticles. Luminescence 24:367–371

27. Polavarapu L, Xu QH (2008) Water-soluble conjugated polymer-induced self-assembly of gold nanoparticles and its application to SERS. Langmuir 24:10608–10611
28. Riboh J, Haes A, McFarland A, Yonzon C, Van Duyne R (2003) A nanoscale optical biosensor: real time immunoassay and nanoparticle adhesion. J Phys Chem B 107:1772–1780
29. Malinsky M, Kelly K, Schatz G, Van Duyne R (2001) Chain length dependence and sensing capabilities of the localized surface plasmon resonance of silver nanoparticles chemically modified with alkanethiol self-assembled monolayers. J Am Chem Soc 123:1471–1482
30. Mestre YF, Zamora LL, Calatayud JM (2001) Flow-chemiluminescence: a growing modality of pharmaceutical analysis. Luminescence 16:213–235
31. Lee SH, Jeon CW, Wabaidur SM (2008) Flow-injection chemiluminescence determination of aspartic acid in tea leaves using tris (2,2′-bipyridyl) ruthenium (ii)–Ce(iv) system. J Fluoresc 18:655–660