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Application of surface plasmon resonance of citrate capped silver nanoparticles for the selective determination of some fluoroquinolone drugs

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ABSTRACT

Citrate capped silver nanoparticles (Ag NPs) was used as a colorimetric probe for the sensitive determination of six drugs belongs to fluoroquinolone family (Ciprofloxacin, Lomefloxacin, Ofloxacin, Pefloxacin, Levofloxacin and Moxifloxacin). The interaction between the studied fluoroquinolones and citrate-capped Ag NPs resulted in the appearance of new surface plasmon resonance (SPR) peaks measured in the range of 598 – 696 nm. Under the optimized conditions, good linear relationships (R^2 = 0.9973–0.9991) were obtained in the range of 1.50–10.25 , 2.0–10.25, 2.0–10.50, 2.0–10.50, 1.5–10.0 and 2.0–11.0 µg/mL for Ciprofloxacin, Ofloxacin, Levofloxacin, Moxifloxacin, Lomefloxacin and Pefloxacin, respectively. The analytical performance of the method was fully validated, and the results were satisfactory. Different pharmaceutical dosage forms containing the cited drugs were successfully analyzed by the suggested method with high degree of accuracy and precision. The proposed method is environmentally safe as it use water as a solvent and does not involve solvent extraction.

INTRODUCTION

Quinolones are a class of broad-spectrum antibiotics, which are active against both gram-positive and gram-negative bacteria. The parent compound of all fluoroquinolones is nalidixic acid. Fluoroquinolones are quinolones derivatives bearing a fluorine atom in the C-6 position. Which has made considerable progress in expanding their spectrum of activity (Kaur *et al.*, 2008). Quinolones rapidly inhibit DNA synthesis by promoting cleavage of bacterial DNA in the DNA-enzyme complexes of DNA gyrase and type IV topoisomerase, resulting in rapid bacterial death (Hooperand Wolfson 1993, Mandell *et al.*, 2000). In the present work, six fluoroquinolone drugs namely; Ciprofloxacin, Lomefloxacin, Ofloxacin, Pefloxacin, Levofloxacin and Moxifloxacin were investigated (Fig. 1).

Many analytical methods were found in literature for detection and determination of the studied antibacterial drugs in bulk, pharmaceutical formulations, and/or in biological fluids. The USP(Rockville 2000) recommends a liquid chromatographic method for determination of ciprofloxacin. A non-aqueous titrimetric method was recommended for ciprofloxacin in USP, Ofloxacin in the BP (Pharmacopoeia, 1998) and Pefloxacin mesylate dihydrate in the European Pharmacopoeia (E.P) (Pharmacopoeia, 1998). The other studied drugs are not official in either pharmacopoeia. Non official methods reported for the determination of the studied drugs included titrimetric (Kiliç *et al.*, 1994; Zhang *et al.*, 1996), spectrophotometric

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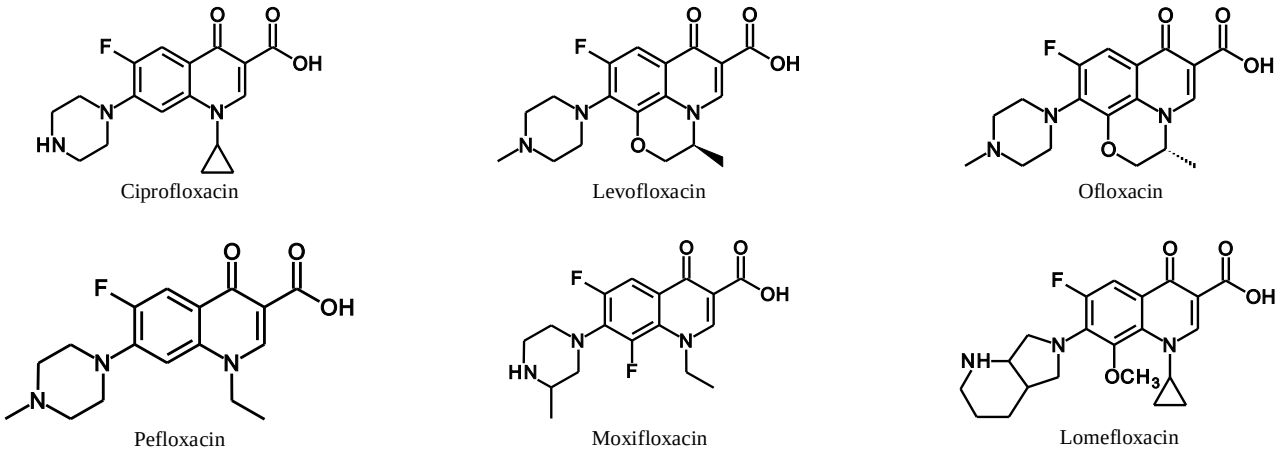


Fig. 1: Chemical structures of the investigated fluoroquinolones.

(Fratiniand Schapoval, 1996; Abdel-Gawad *et al.,* 1998; Rajasekaran *et al.,* 1998; Basavaiahand Prameela, 2002; El-Brashy *et al.,* 2004; El- Brashy *et al.,* 2005; Al- Momani, 2006; Sultan, 2009; Siddiqui *et al.,* 2010; Jain *et al.,* 2011; Ayad *et al.,* 2012; El-Hawaryand Al-Gethami, 2012; Tarkase *et al.,* 2012), Spectrofluorimetric (Jelikić-Stankov *et al.,* 1999; Navalón *et al.,* 2000; Rizk *et al.,* 2000; El-Kommos *et al.,* 2003; Salem, 2005; Kaur *et al.,* 2010; Shah *et al.,* 2013), electrochemical (Belaland El-Din, 1990; Tamer, 1990; Avsecand Gomišček, 1992; Ni *et al.,* 2006), IR (Parent *et al.,* 2004), NMR (Sakai *et al.,* 1999), separation techniques (Wang *et al.,* 1997; Schenckand Callery, 1998; Fierens *et al.,* 2000; González *et al.,* 2005; Gupta *et al.,* 2010; Sousa *et al.,* 2012). Recently, noble metal nanoparticles-based UV–visible spectrometric methods have drawn special attention for selective and sensitive reorganization of target species (inorganic, organic and biomolecules) in various complex matrices (Vilela *et al.,* 2012).

Since, metallic NPs (Au and Ag NPs) are emerging as promising analytical colorimetric reporters for wide variety of analytes because of their intrinsically exploitable properties such as the high extinction coefficient and the distinct variation in color based on their dispersion and aggregation state (Willetsand Van Duyne, 2007; Jain *et al.,* 2008). As a result, noble metallic NPs have been used as promising coloring probes for selective, on-site and real-time colorimetric sensing of a wide variety molecules from various matrices, which facilitates to visualize targets species directly with naked eye (Jain, Huang et al. 2008). Recent years, Ag NPs-based signal amplifications hold great promise in the development of sensitive and selective miniaturized UV–visible approaches for real-time monitoring of trace level target species in complex samples (Ravindran *et al.,* 2013).

For example, Ag NPs are functionalized with various organic derivatives and were used as colorimetric probe for determination of various organic molecules (pesticides, amino acids and DNA) (Thompson *et al.,* 2008; Xiong *et al.,* 2008; Xiongand Li, 2008). Herein, to enhance the sensitivity and selectivity for fluroquinolones determination, we demonstrate the potential use of citrate-capped AgNPs as colorimetric sensor for these drugs. The method is based on the aggregation of citrate-capped Ag NPs induced by the studied drugs.

EXPERIMENTAL

Materials and Reagents

All reagents used were of analytical grade and were used without further purification.

Pharmaceutical grade ciprofloxacin hydrochloride was supplied by Kahira Pharmaceuticals & Chemical Industries Company (Cairo, Egypt). Ofloxacin powder was kindly supplied by the Egyptian International Pharmaceutical Industries Company (EIPICO, Cairo, Egypt), Moxifloxacin hydrochloride was obtained from EVA Pharm. & Chem. Ind. Company (Cairo, Egypt) and Medical Union Pharmaceuticals (MUP, Cairo, Egypt). Levofloxacin hydrochloride was obtained from Memphis Pharmaceuticals & Chemical Industries Co. (Cairo, Egypt). Lomefloxacin hydrochloride by Sigma pharmaceutical Industries (El-Menoufia, Egypt) and Pefloxacin was supplied by Global Napi pharmaceuticals Company, (6^{th} October City, Egypt). Silver nitrate was obtained from Sigma-Aldrich, sodium borohydride ($NaBH_4$) and sodium citrate from Merck (Germany).

Toerell & Stenhagen buffer solution was prepared by mixing the aqueous solutions of; phosphoric acid (3.5 mL /100 mL, El-Nasr chemical company, Cairo, Egypt), citric acid (7 g/100 mL, United company for Chem. & Med. Prep., Cairo, Egypt) and sodium hydroxide (4 g /100 mL, Isochem specifications, Cairo, Egypt). The volume was completed to 1000 mL with distilled water to give buffer stock solution. An appropriate volume from the stock solution was adjusted to the required pH with 0.1 M hydrochloric acid (36%, Lab-Chem fine chemicals & reagents, Cairo, Egypt).

Pharmaceutical formulations

All pharmaceutical preparations were purchased from the local market. Ciprofloxacin tablet: (Amriya Pharm. Ind.,

Alexandria, Egypt) labeled to contain 500 mg Ciprofloxacin per tablet. Venaxan tablet: (SEDICO Pharmaceutical Company, Giza, Egypt) labeled to contain 500 mg Levofloxacin per tablet. Moxacin tablet: (Medical Union Pharmaceuticals MUP, Cairo, Egypt) labeled to contain 400 mg Moxifloxacin per tablet. Maxa-flox tablets: (Pharaonia Pharmaceuticals Company, Alexandria, Egypt) labeled to contain 400 mg Lomefloxacin per tablet. Globacin tablet: (Global Napi pharmaceuticals Company, 6th October city, Egypt) labeled to contain 400 mg Pefloxacin per tablet. Ofloxin tablets: (Kahira Pharmaceuticals & Chemical Industries Company, Cairo, Egypt) labelled to contain 200 mg Ofloxacin per tablet.

Ciprocin eye drop: (the Egyptian International Pharmaceutical Industries Company EIPICO, Cairo, Egypt) labeled to contain 3 mg Ciprofloxacin per 1 ml solution. Maxa-flox eye drop: (Pharaonia Pharmaceuticals Company, Alexandria, Egypt) labeled to contain 3 mg Lomefloxacin per 1 ml solution. Vigamox eye drop: (Alcon, Giza, Egypt) labeled to contain 3 mg Moxifloxacin per 1 ml solution. Ofloxin eye drop: (Kahira Pharmaceuticals & Chemical Industries Company, Cairo, Egypt) labeled to contain 3 mg Ofloxacin per 1 ml solution. Lee-flox eye drop: (SEDICO Pharmaceutical Company, Giza, Egypt) labeled to contain 5 mg Levofloxacin per 1 ml solution. Ciprofloxacin injection for intravenous infusion: (Amriya Pharm. Ind., Alexandria, Egypt) labeled to contain 200 mg ciprofloxacin lactate monohydrate per 100 ml infusion solution. Venaxan injection for intravenous infusion: (SEDICO Pharmaceutical Company, Giza, Egypt) labeled to contain 500 mg Levofloxacin per 100 ml of solution for infusion.

Instrumentation

UV–visible spectra were measured by using Shimadzu UV-1601PC UV-Visible, Scanning Spectrophotometer Detector: Silicon photodiode. All weighing were performed on an electronic single pan balance (Precisa XB 220A, Switzerland)). Distilled water was prepared by water distiller (TYUMEN-MIDI-A0-25 MO, Russia). Boeco magnetic stirrer mms 3000 12 V. 300 mA 0-3000 1/min (Germany) and pH-meter, model AD11P (Adwa, Romania) were used.

Procedures

Preparation of standard solution

Stock solutions containing 300 µg/mL of each fluoroquinolone were prepared in distilled water; Working standard solutions of the appropriate concentrations were prepared by suitable dilution of the stock solutions with distilled water.

Preparation of pharmaceutical samples

Tablets

An accurately weighed amount, equivalent to 12 mg of each drug from composite of 20 powdered tablets, was transferred into a 100-mL calibrated flask and sonicated with about 50 mL of distilled water for 20 min. The solution was diluted to the mark with distilled water and filtered off. further dilutions were made to obtain sample solutions of the required concentrations .

Eye drops and I.V infusion

Specific volumes of drops or I.V. infusion solutions equivalent to 3 mg pure drug were placed in 25 ml volumetric flask and diluted to 25 ml with distilled water. Further dilutions were made to obtain sample solutions of the required concentrations.

Preparation and Characterization of Silver Nanoparticles

Citrate-capped Ag NPs were prepared by the reduction of $AgNO_3$ with $NaBH_4$ as a reducing agent and sodium citrate as a stabilizer, according to the method in the literature (Guo *et al.*, 2008). Briefly, 25 mL of $AgNO_3$ (2.5 mM) was added drop wise to 70 mL of a freshly prepared aqueous solution of $NaBH_4$ (2.5 mM) with vigorous stirring.

After 10 min, 5 mL of sodium citrate solution (1.25 % w/w) was added to stabilize the AgNPs formed. The yellow colloidal solution of Ag NPs was then stirred for another 20 min and aged for 2 days at 4 °C before use. Reaction conditions including stirring time and relative quantities of reagents must be carefully controlled to obtain stable yellow colloidal silver.

If stirring was continued once all of the silver nitrate was added, aggregation began as the yellow solution first turned to darker yellow then violet and eventually grayish after which the colloid broke down and particle settled out.

General Analytical Procedure

A volume of 1 ml of the drug standard or sample solution in the concentration range of 10–110 µg/mL, 1 mL of 0.25 mM prepared AgNPs solution and 1 mL of Toerell & Stenhagen buffer solution (pH 8 for Ofloxacin, Pefloxacin and Levofloxacin and pH 9 for Ciprofloxacin, Lomefloxacin and Moxifloxacin) were added, mixed thoroughly, and allowed to stand for 5 min. The volume was completed to 10 mL with distilled water and the absorbance of the resultant solution was measured at 598, 598, 630, 648, 648 and 696 nm for Ofloxacin, Levofloxacin, Moxifloxacin, Ciprofloxacin, Lomefloxacin and Pefloxacin, respectively. Reagent blank was treated in the same manner replacing the drug with distilled water.

RESULTS AND DISCUSSION

After reduction of Ag^+ ions with sodium borohydride as a reducing agent in the presence of sodium citrate, the solution appeared bright yellow which has a maximum absorption at 397 nm and was attributed to the SPR of monodispersed AgNPs (Qu *et al.*, 2012). This was due to a negative electro-static layer caused by citrate caps on AgNPs, forcing each particle to remain separate of neighboring particles. From the literature (Laliwala *et al.*, 2014), a positively charged molecule can effectively trigger citrate capped nanoparticles to aggregate. Accordingly, fluoroquinolones group can also induce particle aggregation if it has a net positive charge.

Under this assumption, positively charged fluoroquinolones were formed and subsequently interacted with AgNPs.

The dramatic changes of the absorption spectra and solution color of citrate-capped Ag NPs on exposure to six fluoroquinolone drugs (Fig. 2) confirmed that the aggregation mechanism of AgNPs was caused by electrostatic interaction between negatively charged citrate stabilized particle surfaces and the positive charges of fluoroquinolone drug.

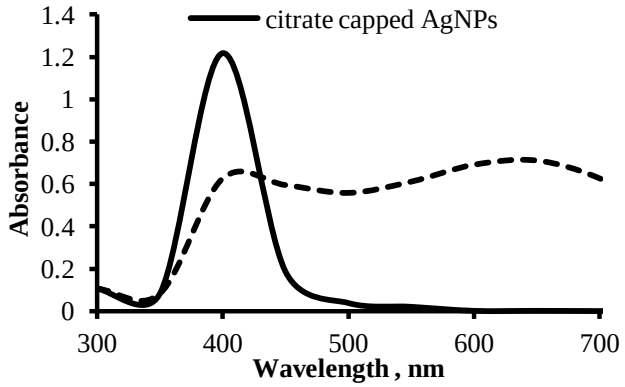


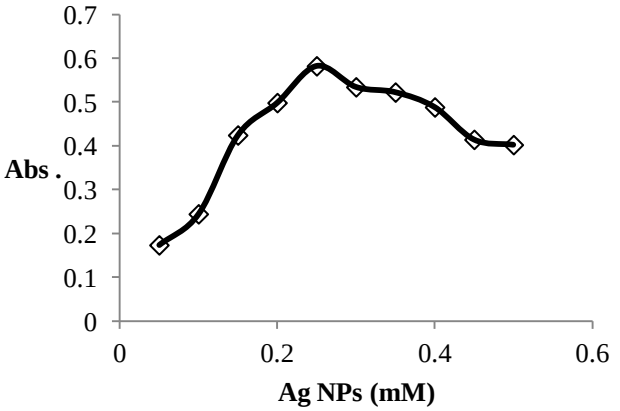
Fig. 2: The absorption spectra of citrate-capped Ag NPs (—) and its reaction product with Ciprofloxacin (- - -).

Optimization of Reaction Conditions

AgNPs have their own unique band, which strongly depends on size, shape, inter-particle distance and the surrounding medium. factors facilitating the SPR change in a presence of target analyte were critically studied.

Effect of Silver nitrate concentration

In this work, the as-prepared AgNPs concentration (calculated based on the final concentration of $AgNO_3$) was 0.25 mM. Suspension of 0.5 mM AgNPs was diluted to 0.05–0.5 mM prior to reaction with studied drugs. The result showed that 0.25 mM AgNPs promoted maximum absorbance and better sensitivity, so this concentration was chosen for the assay procedure (supplementary data, SI 1).



SI 1: The effect of concentration of AgNPs on the SPR absorbance of the reaction between 1 ml of AgNPs (0.05-0.5 Mm) and 1 ml of 7 µg/ml Lomefloxacin (as an example) in the presence of 1 ml of Toerell & Stenhagen buffer solution (pH 9).

Effect of pH

The pH of media did not only influenced the electrical charge of target analyte, but also affect the particle stability(Patel *et al.*, 2015). There is well established study on the agglomeration of metallic NPs surfaces at low pH (< 4), which explains the neutralization of NPs surface charges (aggregation), and resulting a change in their SPR band without addition of analytes(Basu *et al.*, 2007). In order to investigate the best pH for effective colorimetric sensing of fluoroquinolone drugs with citrate-capped Ag NPs, we studied the UV–visible absorption spectra of citrate-capped Ag NPs after the addition of studied drugs at different pH ranges from 4 to 10 (Fig. 3).

Based on the obtained results, we selected pH 8 for Ofloxacin, Pefloxacin and Levofloxacin and pH 9 for Ciprofloxacin, Lomefloxacin and Moxifloxacin as the optimum pH which gave the maximum absorbance and reproducible results. Since, citrate molecules on surfaces of Ag NPs exhibit negative charges, while amino groups of fluoroquinolone drugs bear positive charge, and yielding strong electrostatic interactions between surfaces of Ag NPs and fluoroquinolone drugs, which allow Ag NPs aggregation. As a result, the SPR band at 397 nm was red-shift, and resulting new SPR bands.

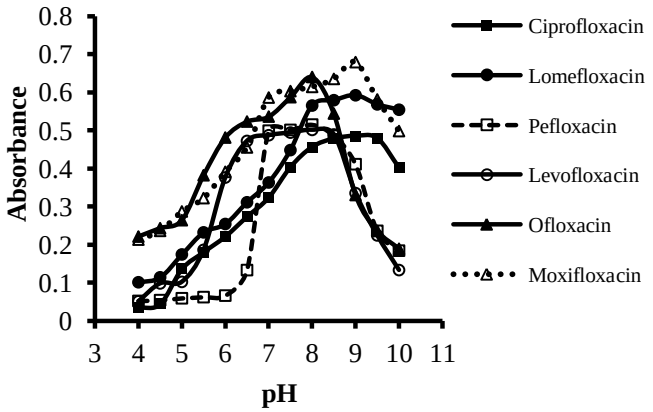


Fig. 3: Effect of pH on the SPR absorbance of the reaction product between 1 ml of AgNPs (0.25 Mm) and 1 ml of 7 µg/ml of fluoroquinolone drugs in the presence of 1 ml of Toerell & Stenhagen buffer solution pH (4-10).

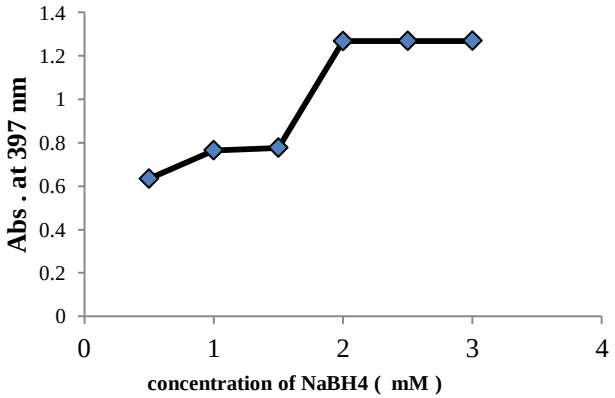
Effect of buffer type and volume

Different types of buffers were used to adjust the pH of the media and their effect on the SPR absorbance of the corresponding reaction was examined.. For example, in the case of Lomefloxacin (7 µg/mL) the obtained absorbance values were 0.272, 0.439, 0.253, 0.204, and 0.586 for phosphate, Britton-Robinson, borate, carbonate and Toerell & Stenhagen buffers, respectively. As the best results was obtained using Toerell & Stenhagen buffer, it was chosen for subsequent study.

The effect of buffer volume on the SPR absorbance of the corresponding reaction was also studied over the volume range 0.2–2.0 mL of Toerell & Stenhagen buffer solution. It was found that 1.0 mL promoted maximum absorbance and better sensitivity (supplementary data, SI 2).

Effect of reducing agent type and concentration

In general, different reducing agents such as ascorbate, $NaBH_4$, elemental hydrogen, polyol process, Tollens reagent and N, N-dimethylformamide (DMF) are used for reduction of silver ions ($Ag^{+)}$ in aqueous or non-aqueous solutions. The aforementioned reducing agents reduce silver ions (Ag^+) and lead to the formation of metallic silver (Ag°), which is followed by agglomeration into oligomeric clusters. These clusters eventually lead to formation of metallic colloidal silver particles (Evanoffand Chumanov 2004, Merga *et al.*, 2007). In case of using $NaBH_4$, as reducing agent, preparation of uniform and size controllable nanoparticles was promoted (Leeand Meisel 1982). Solutions of nanoparticles with various concentrations of $NaBH_4$ were examined. The maximum absorbance of AgNPs at 397 nm was observed in the presence of 2.5 mM $NaBH_4$ solution (supplementary data, SI 3). Thus the synthesis of nanoparticles was done using this amount of $NaBH_4$ solution.



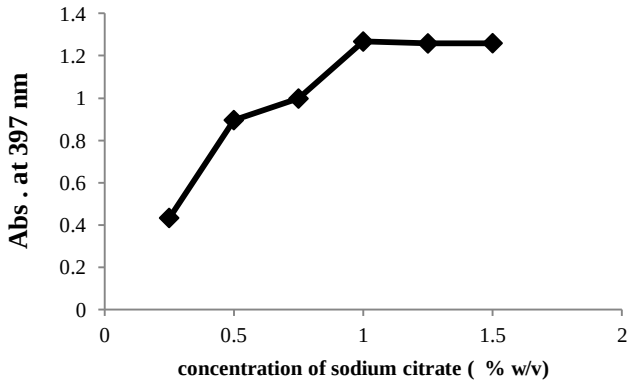
SI 3: Effect of the amount of $NaBH_4$ on the absorption peak of AgNPs.

Effect of stabilizer type and concentration

An important issue in the preparation of metal nanoparticles is the choice of the capping agent used to protect or stabilize the nanoparticle colloidal metals from agglomeration. Size and morphologies of nanoparticles are depending significantly on capping materials. Nanoparticles stabilization is achieved according to the two basic modes: electrostatic and steric stabilization(Oliveira *et al.*, 2005). Electrostatic stabilization is caused by the columbic repulsion between particles, caused by the electrical double layer formed by ions adsorbed at the particle surface (e. g., sodium citrate) and the corresponding counter ions. Steric stabilization is achieved because of the coordination of sterically demanding organic molecules and polymers that act as protective shields on the metallic surface (e. g., PVP). In this study, sodium citrate (which is better used in compare to PVP) was selected as the stabilizer for preventing of silver nanoparticles agglomeration as it causes coulombic repulsion between the nanoparticles and impede the nanoparticles from diffusing together(Templeton *et al.*, 2000).

It should be noted that, the anti-agglomeration role of PVP is due to its steric effect arises from the long polyvinyl chain of this molecule. Decrease or excessive increase in the PVP concentration may cause adverse effects on the dispersion and extinction coefficient of the plasmon band of silver nanoparticles (Zhang *et al.*, 1996). In addition, the amid groups of PVP may cause a change in the free electron density of AgNPs and thus induce a decrease in the extinction coefficient of plasmon band (Carotenuto *et al.*, 2000).

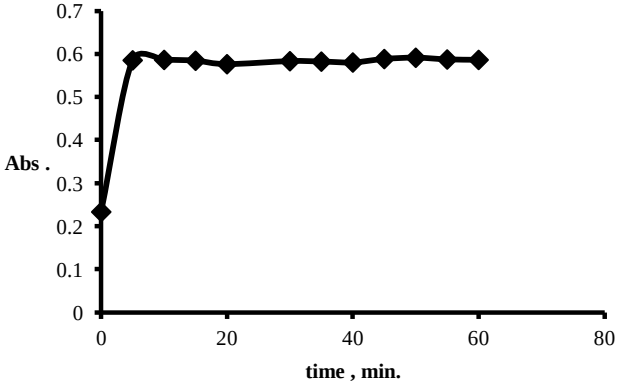
In this study, solutions of nanoparticles with various concentrations of citrate were examined. The maximum absorbance of AgNPs at 397 nm was reached by using 1.25 % sodium citrate solution. Further increase in the percentage of citrate solution did not affect the absorbance (supplementary data, SI 4). Thus the preparation of AgNPs was carried out using this amount of sodium citrate solution.



SI 4: Effect of the amount of sodium citrate solution on the absorption peak of AgNPs**.**

Effect of reaction and standing times

The reaction time of the proposed method was determined by monitoring the SPR absorbance as a function of time, after the colloidal solution was mixed with fluoroquinolone. The SPR absorbance reached a stable maximum within 5 min after the mixing reagents and no significant changes were observed up to 60 min (supplementary data, SI 5). So, the SPR absorbance of all samples was recorded 5 min after preparation of the solutions.



SI 5: Effect of reaction time on the SPR absorbance of the corresponding reaction. Condition: 1ml of AgNPs (0.25 mM), 1 ml of 7 µg/ml Moxifloxacin (as an example) and 1 ml of Toerell & Stenhagen buffer solutions pH 8.

Validation of the proposed methods

The developed procedure was fully validated according to International Conference on Harmonisation guidelines (Branch 2005) in respect to linearity, range, accuracy, precision.

Linearity and range

Under the described experimental conditions , standard calibration curves for the determination of investigated fluoroquinolones with proposed AgNPs method were constructed by plotting absorbance against concentration. Linear relationships with correlation coefficients in the range of 0.9973-0.9991 were obtained. The linear concentration ranges were 1.50–10.25, 2.0–10.25, 2.0–10.50, 2.0–10.50, 1.5–10.0 and 2.0–11.0 µg/mL for Ciprofloxacin, Ofloxacin, Levofloxacin, Moxifloxacin, Lomefloxacin and Pefloxacin, respectively. Other statistical parameters such as; correlation coefficients, intercepts, slopes detection and quantification limits are listed in (Table 1).

Accuracy and Precision

The accuracy of the method was checked by applying the general analytical procedure for the determination of the investigated drugs in three replicates at three different concentrations. The results obtained (Table 2) showed the close agreement between the measured and true values as the values of the % recovery is close to 100%.

In addition, the low values of standard deviations indicated the good precision of the proposed method. The repeatability (intra-day precision) of the proposed method was checked through performing replicate analysis of the drug in pure form on three successive times. While intermediate precision (inter-day precision) was performed through repeated analysis, using the same concentration level in three successive days. The results are summarized in (Table 3) which show low values of relative standard deviations (not exceed 2%). This gives an indication of the high precision of the proposed method.

Selectivity and effect of Interferences

In order to evaluate of the selectivity of the proposed method for the analysis of pharmaceutical preparations containing the selected fluoroquinolones, the interferences effect of various pharmaceutical additives such as glucose, lactose, fructose, maltose, sucrose and magnesium stearate was studied. Solutions containing Pefloxacin (7.0 µg/mL) as a representative example in the presence of one of the pharmaceutical additives (20 µg/mL) were analyzed with the proposed method. It was found that there was no significant interferences effect was observed by the studied excipients on the results of the method (Supplementary data, SI 5).

Quantitation and detection limits

Sensitivity of the proposed method was checked by calculating the detection (LOD) and quantitation (LOQ) limits using the formula; LOD=3.3xSa/b and LOQ=10xSa/b, where Sa is the standard deviation of blank and b is the slope of the calibration curve. The calculate LOD values were in the range of 0.25 – 0.44 µg/mL while LOQ values are in the range 0.75 – 1.31 µg/mL of the studied drugs (Table 1). This confirm the enhanced sensitivity of the suggested procedure compared to the previously reported spectrophotometric methods.

Table 1: Analytical parameters for determination of the investigated drugs by the proposed method.

Drug	λ_{max} (nm)	Linear range [a]	Slope	Intercept	r [b]	LOD#	LOQ#
Ciprofloxcin	648	1.75-10.25	0.071	0.005	0.9978	0.35	1.04
Ofloxacin	598	2.00-10.25	0.093	0.082	0.9974	0.42	1.26
Levofloxacin	598	2.00-10.50	0.095	0.066	0.9973	0.44	1.31
Moxifloxacin	630	2.00-10.50	0.101	0.037	0.9991	0.25	0.75
Lomefloxacin	648	1.50-10.00	0.082	0.008	0.9980	0.37	1.10
Pefloxacin	696	2.00-11.00	0.072	0.013	0.9984	0.34	1.02

[a] The concentration is in µg/ml.
[b] LOD; limit of detection, LOQ; limit of quantitation, and r; correlation coefficient.

Table 2: Evaluation of accuracy of the analytical procedure of the studied drugs.

Drugs	% Recovery [a]			
	4.00 µg/ mL	6.00 µg/ mL	8.00 µg /mL	Mean ± SD#
Ciprofloxacin	98.32	98.73	101.25	98.40±1.60
Ofloxacin	101.39	98.67	99.26	99.77±1.43
Pefloxacin	100.38	102.01	98.32	100.24±1.85
Levofloxacin	99.02	101.79	100.25	99.50±1.39
Moxifloxacin	102.86	100.41	99.34	100.89±1.80
Lomefloxacin	96.96	98.93	99.53	98.47±1.34

[a] Average of three determinations, # SD Standard deviation.

Table 3: Evaluation of intra- and inter-day precision of the analytical procedure of the studied drugs (6.0 µg/mL).

Drug	% Recovery* ± RSD [a]	
	Intra-day precision	Inter-day precision
Ciprofloxacin	99.76 ± 1.76	99.45± 0.73
Ofloxacin	100.30 ± 0.61	99.14± 1.42
Lomefloxacin	100.08 ± 0.58	100.01± 0.49
Levofloxacin	99.98 ± 1.08	100.58± 0.81
Moxifloxacin	100.58 ± 0.81	99.99± 0.21
Pefloxacin	100.78± 1.12	99.73± 1.69

[a] Average of three determinations, RSD is Relative standard deviation.

Table 4: Analysis of the studied fluoroquinolones in its pharmaceutical formulations using the proposed and reported methods.

Dosage forms	Drug (conc.)	% Recovery [a] ± SD		t-test	F-value
		Proposed method	Reported method		
Ciprocin eye drop	Ciprofloxacin (3 mg/1 ml)	100.86±1.53	99.43±1.10[32]	1.32	1.93
Ofloxin eye drop	Ofloxacin (3 mg/1 ml)	101.38±0.56	100.51±0.67	0.53	2.71
Lee-flox eye drop	Levofloxacin (5 mg/1 ml)	101.00±0.83	100.33±1.10	0.84	1.76
Ciprofloxacin injection (I.V)	Ciprofloxacin (200 mg/100 ml).	100.25±0.82	100.11±0.72	0.23	1.30
Venaxan injection (I.V)	Levofloxacin (500 mg/100 ml)	100.95±1.06	100.02±1.34	0.94	1.60
Maxa-flox eye drop	Lomefloxacin (3 mg/1 ml)	99.47±1.09	99.97±1.55 [33]	0.46	2.02
Vigamox eye drop	Moxifloxacin (3 mg/1 ml)	99.45±0.73	100.94±1.07[34]	1.99	2.15

[a] Theoretical value at 95% confidence limit; F= 3.18 and T =2.78.

SI 6: Effect of presence of commonly used excipients on the determination of Pefloxacin (7.0 µg/mL) as representative example.

Excipients (20 µg/mL)	Recovery (%)
Glucose	99.22 ± 0.97
Sucrose	100.30 ± 0.61
Fructose	100.29 ± 0.93
Maltose	100.70 ± 0.84
Lactose	99.47± 1.21
Magnesium stearate	100.69 ± 0.69

Application to pharmaceutical dosage forms

Finally, the proposed method has been applied in determining the studied drugs in commercial tablets , eye drops and I.V Infusion. The results were compared statistically with those of the reported methods using student`s t- and F- tests at the 95% confidence level (Table 4).

The absence of any significant difference between the calculated and theoretical values of both t- and F-values indicated good levels of accuracy and precision of the proposed method, respectively. The sensitivity, simplicity and minimal volume of samples make the method suitable for routine analysis in quality control laboratories.

CONCLUSION

In this work, we described the use of citrate-capped AgNPs as colorimetric probe for determination of six fluoroquinolone drugs (Ciprofloxacin, Lomefloxacin, Ofloxacin, Pefloxacin, Levofloxacin and Moxifloxacin).

The binding action between the ligands of citrate capped Ag NPs and fluoroquinolone drugs led to significant red-shift in the absorption spectra with concomitant visible color changes from yellow to blue. The method offers several advantages over the previously reported analytical techniques for the studied drugs.

From economic point of view, the proposed method is simple, rapid and inexpensive as it is less time-consuming and does not require various elaborate treatment or tedious extraction procedures. From environmental point of view, the proposed method is environmentally safe since water is the reaction solvent which is the most important green solvent and volatile solvents are omitted in the present work. Additionally, the method was successfully validated to quantify the fluoroquinolone drugs in pharmaceutical preparations. It could be concluded that this approach has great potentiality for the detection of studied fluoroquinolones in pharmaceutical samples with high accuracy and precision.

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