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Chitosan Capped Silver Nanoparticles as Colorimetric Sensor for the Determination of Iron(III)

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A selective, simple and low-cost method for the colorimetric determination of Fe^{3+} ions based on chitosan capped silver nanoparticles (Chit-AgNPs) is presented. Chitosan is a cationic polyelectrolyte possessing amino and hydroxy groups which make it widely used as a capping agent for Ag NPs. The synthesized chitosan capped silver nanoparticles with excellent colloidal stability were characterized by UV-Vis spectrometry, transmission electron microscopy, Fourier transform infrared, and X-ray diffraction. Chit-AgNPs exhibit a strong surface plasmon resonance band which disappears in the presence of increasing concentrations of Fe^{3+} ions. This system showed a visually detectable color change from brownish-yellow to colorless for the selective determination of Fe^{3+} . The method can be applied for the determination of Fe^{3+} ions in the concentration range of 1.0×10^{-6} - 5.0×10^{-4} M. The detection limit was determined from three times the standard deviation of the blank signal ($3\sigma/\text{slope}$) as 5.3×10^{-7} M. The developed method was successfully applied for the determination of Fe^{3+} in real samples

Keywords: Chitosan capped silver nanoparticles, Colorimetric determination, Iron(III) ion

INTRODUCTION

Metallic nanoparticles due to their physicochemical and biological properties that are highly correlated with their small sizes and high surfaces have important applications in nanotechnology [1-3]. Silver nanoparticles (AgNPs) have significant application in various fields because of their optical, electronic, anti-microbial, sensor, catalytic and thermal properties [4-9]. Despite the diversity in techniques employed to produce AgNPs, developing a clean and non-toxic medium for the synthesis of this metallic nanoparticles is of paramount importance. The most common technique for preparing silver nanoparticles is based on the chemical reduction of a silver salt. These methods are simple and effective, however, the removal of the agents used and biological toxicity of the remaining agents are of the known disadvantages for these methods [10]. Thus, there is an interest in using dispersing or reducing agents based on

biomaterial systems [11]. Some of the materials have been used to bind silver on various materials, such as silane [12], and chitosan [13]. Zhu *et al.* immobilized silver onto the surface of a chitosan membrane through the coordination between silver ions and the amino groups of chitosan [13].

Chitosan, next to cellulose, is the second most abundant biomass which has a reiteration structure of (1,4)-linked 2-amino-2-deoxy-b-D-glucan. This is known as a biocompatible, biodegradable, almost nontoxic material [14] and also a conductor polymer commonly used to elevate the stability of nanoparticles of silver [10], copper [15], iron [16], iron oxide [17], gold [18], platinum and palladium [19] as well as bimetallic nanoparticles [20]. Because of the presence of reactive amino and hydroxyl functional groups in its structure, chitosan is considered as a triple purpose agent. First, chitosan is chosen to immobilize silver nanoparticles because chitosan molecule contains nitrogen atoms that can bind silver ion to form a complex [21]. Second, since chitosan molecule includes a large number of reactive hydroxyl groups, it could be used to modify the

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surface hydrophilicity of the membranes [22]. Third, the antibacterial properties and nontoxicity, high mechanical strength and hydrophilicity of chitosan were well registered [23-25].

Metal ions play an important role in many chemical reactions such as biological metabolisms as well as many other processes [26-29]. Among various trace elements, Fe^{3+} is an essential transition metal in many enzymatic electron transfers and oxidation reactions [30]. Although chemosensors of metal ions have been recently developed, [31], their design for the detection of metal ions is still an active area of research [32,33]. Because of the importance of the determination of iron ion in the environmental and biological analyses [34] the development of an analytical method for the sensitive and selective determination of Fe^{3+} is highly desirable [35,36].

In this study, a simple, facile, low-cost and efficient selective optical chemosensor is presented for Fe^{3+} ion based on the chitosan capped silver nanoparticles. It was found that the surface plasmon resonance (SPR) intensity of the as-synthesized Ag nanoparticles decreases when Fe^{3+} ions are added into the solution. Moreover, the color of the Ag nanoparticles solution showed a change upon addition of different concentrations of Fe^{3+} . On the basis of the SPR intensity of the silver nanoparticles, the sensitive detection of Fe^{3+} has been successfully realized.

EXPERIMENTAL

Materials and Solutions

Silver nitrate (AgNO_3), sodium borohydride (NaBH_4) and hydrazine were purchased from Merck. Chitosan was purchased from Aldrich. All chemicals were of analytical grade and used without further purification. Solutions of KNO_3 , NaNO_3 , $\text{Al}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, CdSO_4 , MnSO_4 , FeSO_4 , $\text{Zn}(\text{NO}_3)_2$, $\text{Mg}(\text{CH}_3\text{COO})_2$, $\text{Ba}(\text{NO}_3)_2$, KNO_3 , MnSO_4 and $\text{Fe}(\text{NO}_3)_3$ were prepared. All the metal salts used for the experiments were purchased from Merck. Milli-Q-purified water was used for sample preparations. These solutions were used for all spectroscopic studies after appropriate dilution. Sulfuric acid (0.1 M) and sodium hydroxide (1.0 M) were used to adjust the pH.

Apparatus

The UV-Vis absorbance spectra were recorded on a Unico UV-Vis spectrophotometer at room temperature using quartz cells with 1.0 cm path length. Measurements of pH were made with a Denver Instrument Model 780 pH meter equipped with a Metrohm glass electrode. Transmission electron micrograph (TEM) was taken with Zeiss-EM10C-80 KV and XRD spectra were obtained by D8ADVANCE type (BRUKER-Germany). Fourier transform infrared spectroscopy (FT-IR) measurements were performed with a Spectrum RX1 (Perkin Elmer, 940 Winter Street, and Waltham, Massachusetts 02451, USA).

Synthesis of Chitosan-Capped Silver Nanoparticles

Chitosan-capped silver nanoparticles (Chit-AgNPs) were synthesized through a classic reduction method [37] based on the reduction of AgNO_3 by NaBH_4 in the presence of chitosan, acting as stabilizing and protecting agent as well. In particular, 25.0 mg chitosan was dissolved in 50.0 ml 4% acetic acid and was sonicated for 5 min. Then, 20.0 ml of this solution was added to 50.0 ml aqueous solution of AgNO_3 (6.0 mM) and the reaction was performed at room temperature under vigorous magnetic stirring for 30 min. Then, an aqueous solution of NaBH_4 (1.0 ml, 58.0 mM) was added dropwise. The solution first turned into yellow, then brown, and finally became a brownish-yellow suspension. Stirring was maintained for 2 h to ensure full reaction. The chitosan-capped silver nanoparticles, which form stable dispersions in water without introducing additional stabilizers, were kept at room temperature.

Procedure

In a general procedure, under optimum conditions, 200.0 μl aqueous solution of chitosan-capped silver nanoparticles (Chit-AgNPs) was added to 3.0 ml sulfuric acid (pH = 2.0) solution, followed by addition of Fe^{3+} ion solutions. Then, the change in the absorbance of the solution was recorded at 398 nm.

RESULTS AND DISCUSSION

Characterization of Chitosan-Capped Silver Nanoparticles

The synthesized silver nanoparticles were characterized

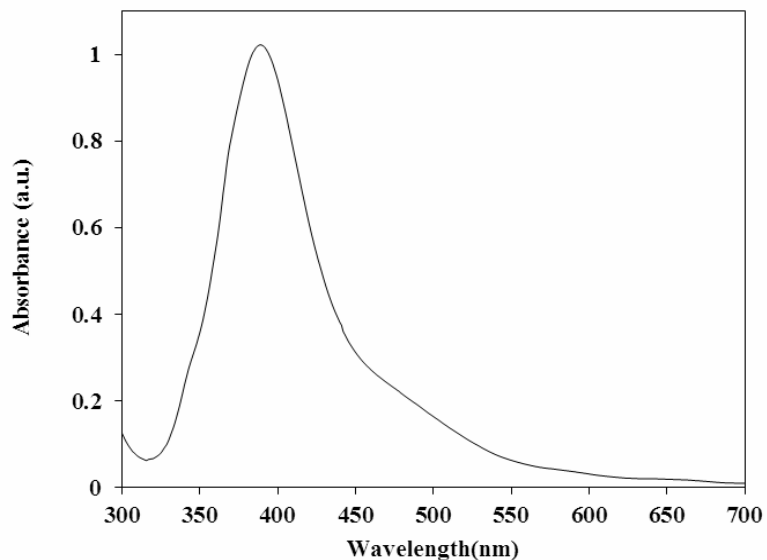


Fig. 1. The UV-Vis spectrum of Chit-AgNPs.

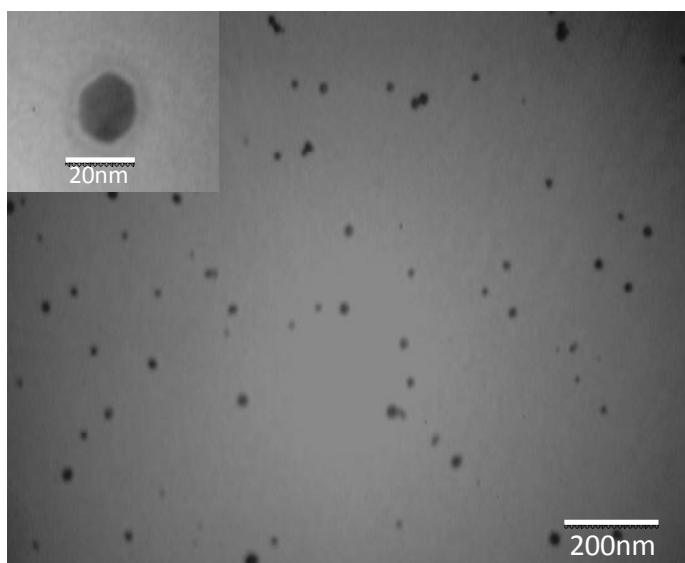


Fig. 2. The TEM images of Chit-AgNPs.

by TEM, FT-IR, XRD and UV-Vis spectroscopy. The UV-Vis spectrum of the dispersed silver nanoparticles in water is shown in Fig. 1. The λ_{max} of silver nanoparticles was observed around 398 nm which is the characteristic surface plasmon resonance (SPR) band of silver nanoparticles. The formation of silver nanoparticles was further confirmed by

TEM analysis. The TEM image (Fig. 2) shows that Chit-AgNPs are uniformly dispersed in aqueous solution with an average diameter of 15 nm.

Fourier transforms infrared (FT-IR) spectra of chitosan and chitosan-capped silver nanoparticles, respectively, are shown in Figs. 3a and b. The band at 3410 cm^{-1} indicates

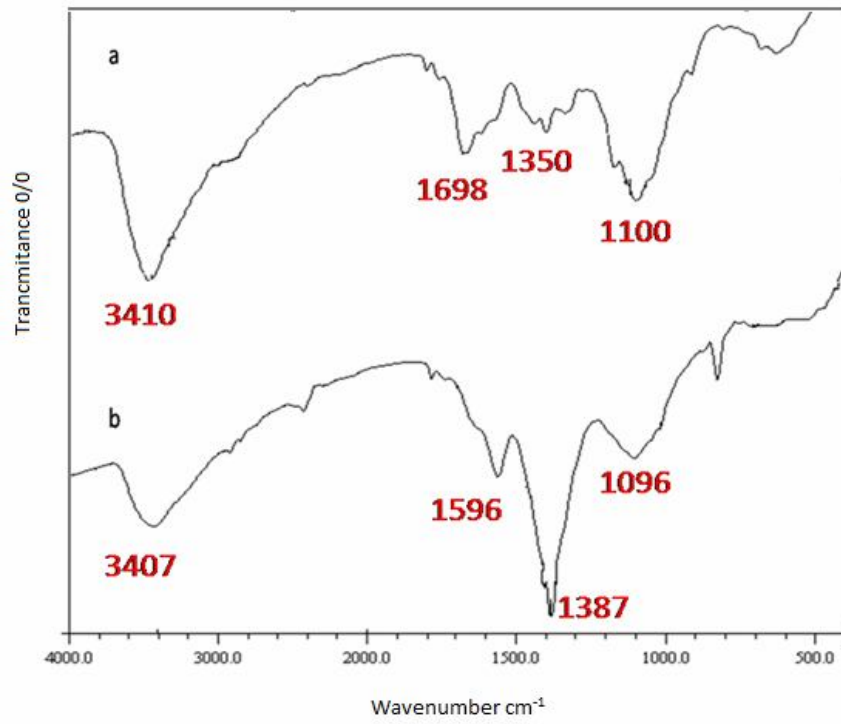


Fig. 3. The FT-IR spectra of (a) Chitosan, (b) Chit-AgNPs.

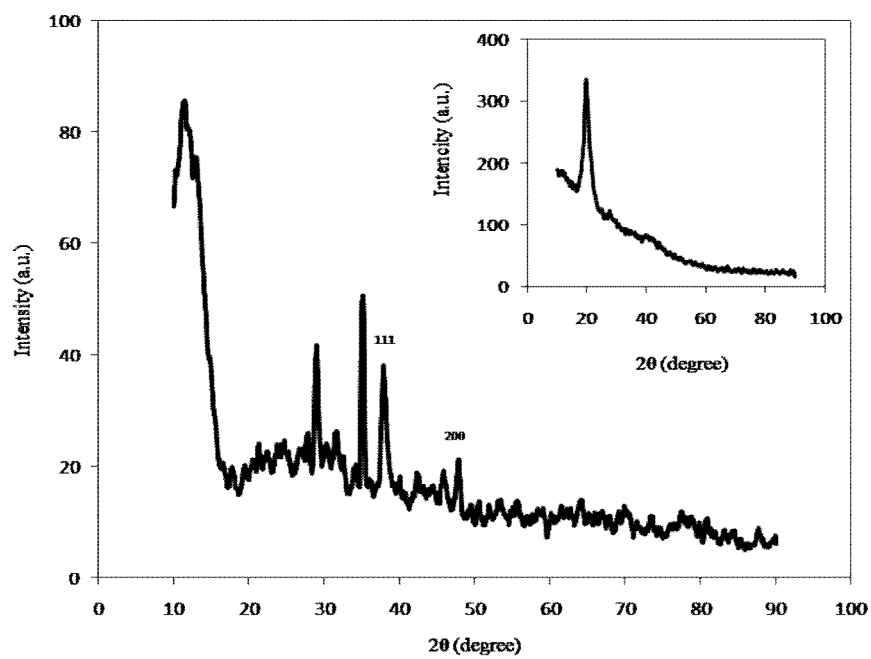


Fig. 4. The XRD patterns of Chit-AgNPs and chitosan (inset).

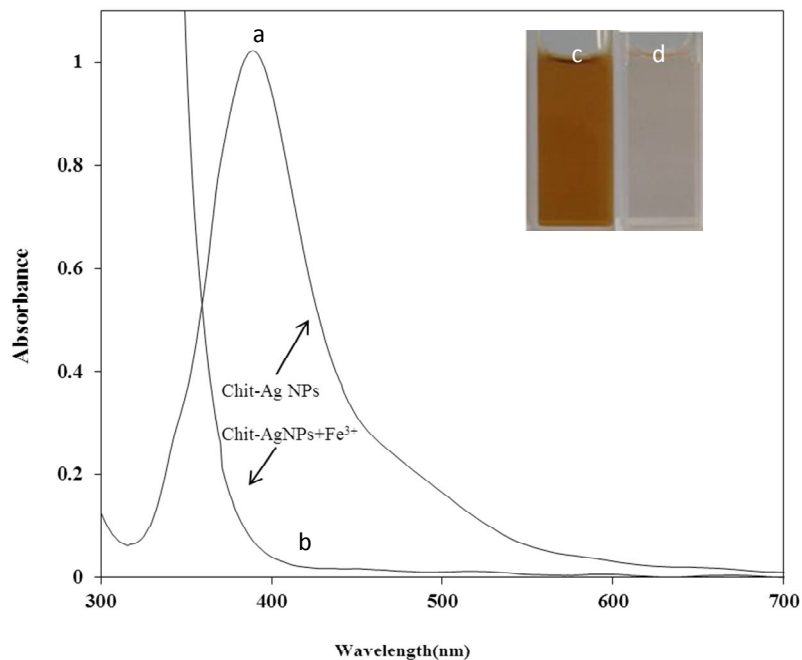


Fig. 5. a) UV-Vis spectra of Chit-AgNPs and b) Chit-AgNPs with Fe³⁺, c) and d) the color changes of silver nanoparticles in the absence and presence of 5.0×10^{-4} M Fe³⁺ ions, respectively.

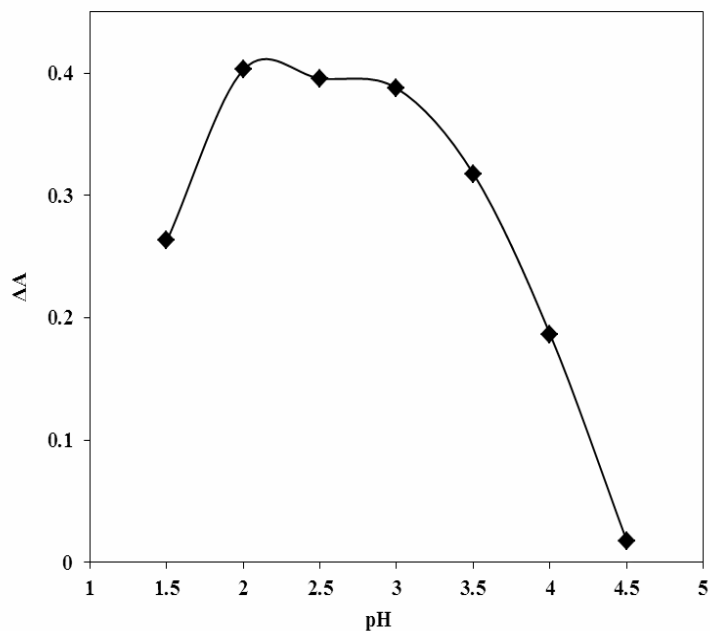


Fig. 6. Effect of the solution pH on the response of colorimetric sensor, experimental conditions: 2.0×10^{-4} M of Fe³⁺, pH range of 1.5-4.5 and response time of 6 min.

the combined peaks of the NH_2 and OH group stretching vibration in chitosan. The peak at 1100 cm^{-1} is related to C-O stretching and that of N-H bending is observed at 1698 cm^{-1} . The peak intensity in 1387 cm^{-1} is due to C-N stretching in chitosan-capped silver nanoparticles because of the complexation of chitosan with silver. This indicates the binding of Ag with O and N of -OH and $-\text{NH}_2$ groups [38]. Chitosan-capped silver nanoparticles and chitosan were also characterized by XRD and the results are shown in Fig. 4. This figure shows two peaks at 2θ equal to about 38.5° and 45.6° which are assigned to the (111) and (200) planes of a face-centered cubic (fcc) silver crystal and there is a peak at $2\theta = 21.8^\circ$ (Fig. 4 inset) which is assigned to chitosan. The diffraction peaks at 29.5° and 32.6° can be attributed to AgNO_3 residuals [39]. There is a weak peak in the diffractogram of chitosan at 21.8° indicating a high degree of crystallinity of chitosan [33].

Spectrophotometric Studies

The UV-Vis spectrum of the dispersed silver nanoparticles in the absence and presence of Fe^{3+} ions is shown in Figs. 5a, b. The λ_{max} of chitosan-capped silver nanoparticles was observed around 398 nm. This is the characteristic surface plasmon resonance (SPR) band of silver nanoparticles. It was found that Chit-Ag nanoparticles responded to Fe^{3+} with a dramatic color change from brownish-yellow to colorless, which could be easily detected by the naked eye. The Figs. 5c, d shows the color changes of silver nanoparticles in the absence and presence of Fe^{3+} ions, respectively.

Here a new sensing protocol based on the optical characteristics of the synthesized Chit-AgNPs response towards Fe^{3+} detection is introduced in Scheme 1 [40]. When Fe^{3+} ions were introduced to the Chit-AgNPs solution, the gradual decrease of SPR intensity depended on the Fe^{3+} concentration. This decreased SPR intensity is presumably due to the weak coordinating interaction of Fe^{3+} ions on the individual AgNPs surface with the $-\text{NH}_2$ and -OH groups of the capped chitosan that causes the donation of electron density from the AgNPs system to the metal ions [41].

Effect of pH

In order to find the best pH for effective colorimetric

sensing of Fe^{3+} with chitosan-capped AgNPs, the UV-Vis absorption spectra of chitosan-capped AgNPs was investigated by the addition of Fe^{3+} at different pH ranges from 1.5-4.5 and the results are shown in Fig. 6. It was found that at pH 2.0, in sulfuric acid solution, there was a maximum change (ΔA : absorbance changes) in the optical density. At pH less than 2.0 the positive charge due to the protonation of chitosan [42-43] inhibits the interaction between iron(III) ions and chitosan. Also, at pH higher than 3.8, the hydrolysis of Fe^{3+} and $\text{Fe}(\text{OH})_3$ formation was observed. Therefore, pH = 2.0 was chosen for adjusting the pH of Fe^{3+} solution samples.

Effect of AgNPs Volume

The UV-Vis absorbance of the Chit-AgNPs system is highly dependent on the Chit-AgNPs concentration. To find the optimum Chit-AgNPs concentration for the determination of Fe^{3+} , the effect of Chit-AgNPs concentration on UV-Vis absorbance was investigated and the results are shown in Fig. 7. The absorbances of a series of solutions containing $2.0 \times 10^{-4}\text{ M Fe}^{3+}$ and various amounts of Chit-AgNPs in sulfuric acid were measured. It was found that 200.0 μl Chit-AgNPs is sufficient. Hence, 200.0 μl of Chit-AgNPs solution was adopted in further studies.

Effect of Reaction Time

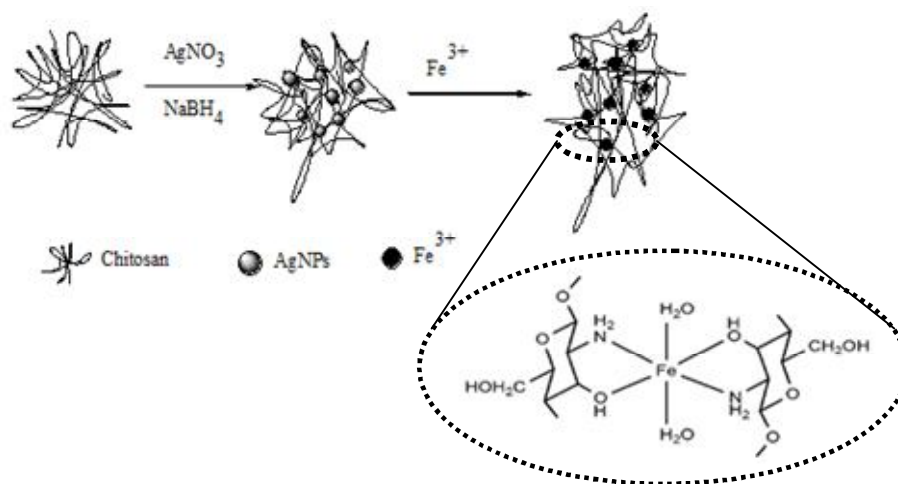
The effect of the reaction time on the difference of the absorption peak of Chit-AgNPs in the absence and presence of Fe^{3+} ion was investigated. It was found that the reaction time depends on the concentration of Fe^{3+} ion. Figure 8 shows that in $2.0 \times 10^{-4}\text{ M Fe}^{3+}$ the signal reaches to 95% after 6 min and at high concentrations of Fe^{3+} from $2.0 \times 10^{-4}\text{ M}$, higher rapid response time is achieved.

Stability of Chit-AgNPs

The UV-Vis spectra of Chit-AgNPs, six months after preparation, was compared with freshly prepared sample and the spectra were shown in Fig. 9a, and b, respectively. The results show that Chit-AgNPs remain stable for at least 6 months.

Interferences of Foreign Ions

The absorption spectrum of the chitosan-capped AgNPs



Scheme 1. The processes of formation of the Chit-AgNPs nanoparticles and the sensing mechanism for Fe^{3+} ions

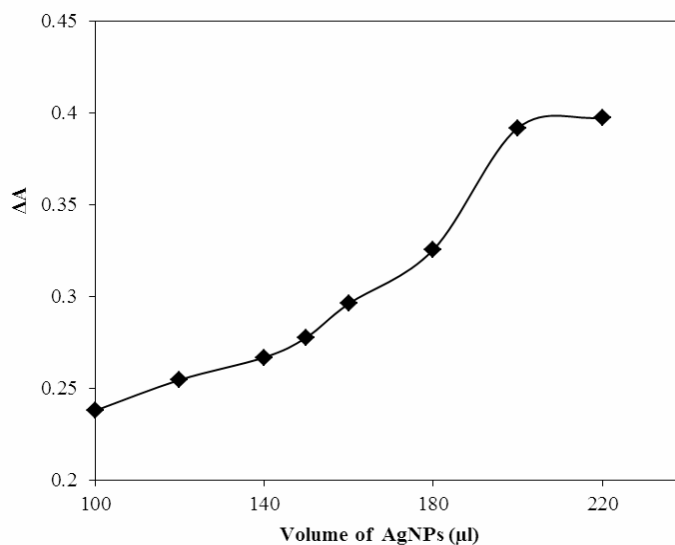


Fig. 7. Effect of the Chit-AgNPs concentration on the response of the sensor, experimental conditions: 2.0×10^{-4} M of Fe^{3+} , pH 2.0 in sulfuric acid solution and response time of 6 min.

was recorded in the presence of different metal ions to investigate the selectivity of the sensor. The recognition profiles of chitosan-capped silver nanoparticles toward various metal cations: Fe^{3+} , Fe^{2+} , Ni^{2+} , Mn^{2+} , Al^{3+} , Co^{2+} , Cu^{2+} , Na^+ , K^+ , Cd^{2+} and a mixture of total ions were primarily investigated by UV-Vis spectrophotometry in sulfuric acid. However, interferences from coexisting ions

were examined, and the results are shown in Figs. 10a, b. Mn^{2+} , Al^{3+} , Co^{2+} , Cu^{2+} , Na^+ , K^+ and Cd^{2+} gave no interferences at the concentration level of 1.9×10^{-2} M (100 fold excess of Fe^{3+}) and Fe^{2+} , Ni^{2+} gave no interferences at the concentration level of 1.9×10^{-3} M (10 fold excess of Fe^{3+}) when the determined Fe^{3+} concentration was 1.9×10^{-4} M. Moreover, the examined metal ions had no effects on the

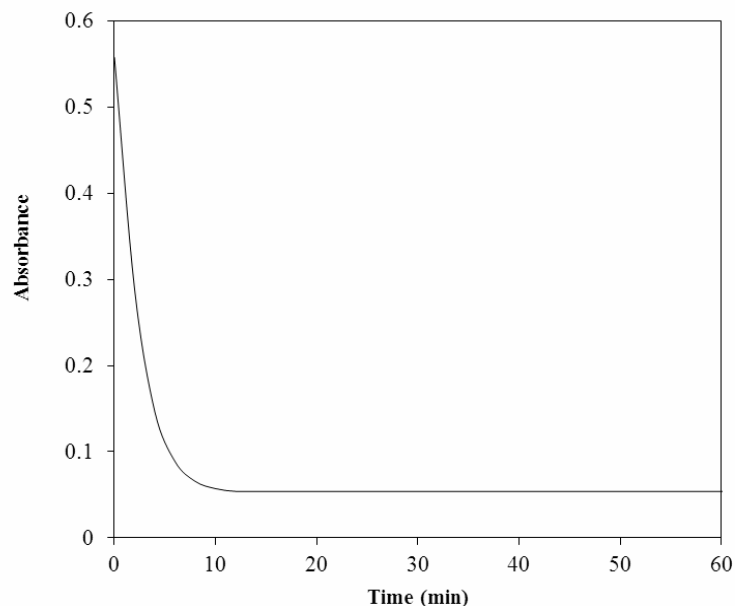


Fig. 8. Reaction time of the colorimetric sensor for $2.0 \times 10^{-4} \text{ Fe}^{3+}$.

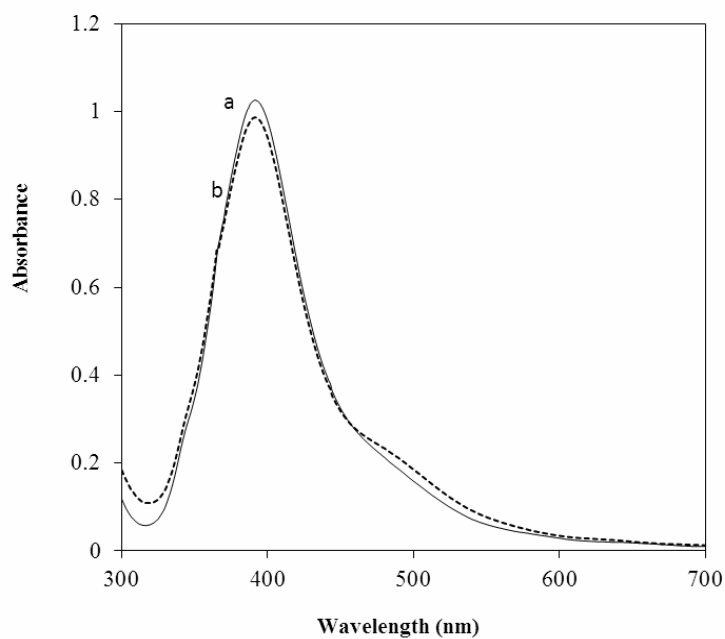


Fig. 9. The UV-Vis absorption spectra of a) the newly synthesized Chit-AgNPs and b) the Chit-AgNPs stored for six months.

absorption spectra of Chit-AgNPs under the same condition and the results indicate that Chit-AgNPs was a selective colorimetric sensor for Fe^{3+} ion.

Calibration Curve and Detection Limit

Figure 11 represents changes in the absorption spectra of the Chit-AgNPs solution after addition of different

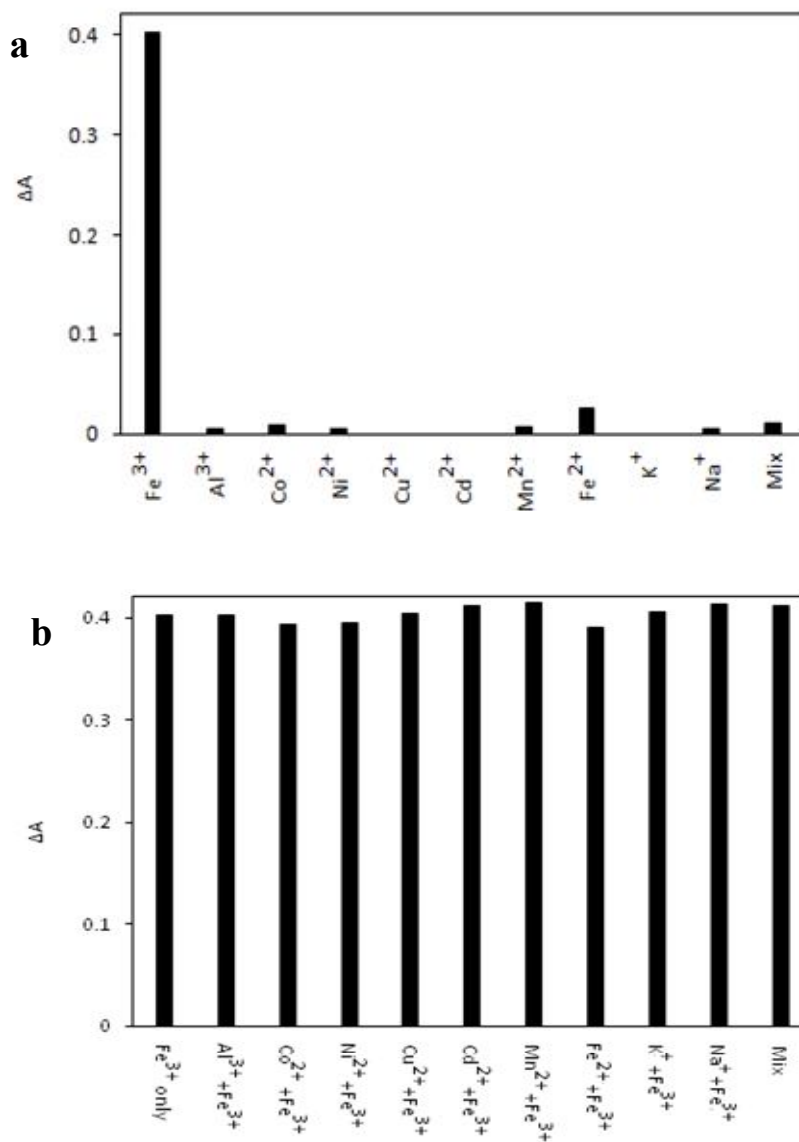


Fig. 10. Response of the sensor for detecting Fe³⁺ in the absence (a) and presence (b) of equimolar concentration of different metal ions for selectivity investigation.

concentrations of Fe³⁺. A linear correlation exists between ΔA (absorbance changes) and the Fe³⁺ concentration over the concentration range of 1.0×10^{-6} - 5.0×10^{-4} M. The calibration equation is as: $\Delta A = 1793.9 C (M) + 0.0465$ ($R^2 = 0.9902$). The detection limit of the nanosensor for the analysis of Fe³⁺ was determined from three times the standard deviation of the blank signal ($3\sigma/\text{slope}$) which was found to be 5.3×10^{-7} M.

Table 1 summarizes the reported sensing probes for Fe³⁺ detection. It can be seen that the Chit-AgNPs sensor exhibits a LOD lower than that in most reported systems.

Real Samples Analysis

To evaluate the analytical applicability of the developed method, it was applied for determination of Fe³⁺ in boiler water (taken from Shiraz Power Plant, Iran) and waste water

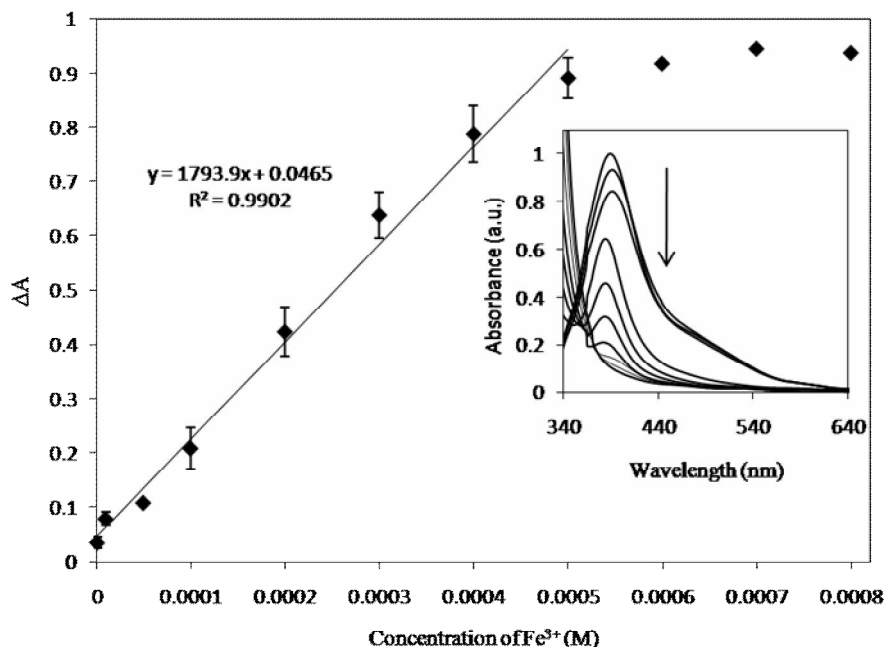


Fig. 11. Calibration curve for chitosan-capped AgNPs in the presence of different concentrations of Fe^{3+} ion.

Table 1. The Comparison of the LOD and Linear Range between Different Works for the Determination of Fe^{3+}

Reagent	Linear range (μM)	Limit of detection (μM)	Ref.
GO nanosheets	0.12-1.20	17.90	[44]
S-GODs	0.01-0.70	0.0042	[45]
Rhodamine B Schiff-base	1.00-18.00, 5.00-40.00	0.11, 0.16	[46]
GQDs	0.00-400.00	7.22	[47]
Gold nanoparticles	10.00-60.00	5.60	[48]
Chit-AgNPs	1.00-500.00	0.53	This work

GO: Graphene oxide. S-GQDs: Sulfur-doped graphene quantum dots. GQDs: Graphene quantum dots. Chit-AgNPs: Chitosan-capped silver nanoparticles.

samples. To do this, 5.0 ml of the sample, without any pretreatment, were spiked and the experimental results were taken and listed in Table 2. The recoveries of Fe^{3+}

concentration are between 96% and 102%, indicating that the method can be applied for the determination of Fe^{3+} in real samples with satisfactory results.

Table 2. Determination of Fe³⁺ in Real Sample Using Chit-AgNPs

Sample	Added (μM)	Found (μM)	Recovery (%)	RSD (%)
Boiler water	0.0	ND ^a	-	2.6
	10.0	10.2	102.0	3.1
	106.0	104.0	98.1	4.6
	200.0	192.0	96.0	3.3
Waste water	0.0	5.7	-	3.6
	10.0	15.95	102.5	4.1
	50.0	56.3	101.2	3.4
	100.0	104.6	98.9	2.9
	200.0	198.5	96.4	4.2

^aNot detect.

CONCLUSIONS

A simple, facile, low-cost and efficient selective optical chemosensor was presented for Fe³⁺. The distinct color change of Chit-AgNPs can be detected by naked eyes. The as-prepared chitosan-capped silver nanoparticles showed excellent colloidal stability. The method showed relatively good selectivity for Fe³⁺ with the lowest detection concentration of 0.53 μM . The developed method was successfully applied to determine Fe³⁺ in real samples.

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