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## **Development of a New Fluoride Colorimetric Sensor Based on Anti-aggregation of Modified Silver Nanoparticles**

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In this study, aggregated silver nanoparticles were prepared using sulphanic acid and catechol as a collection of stabilizing-reducing system. Preliminary studies showed that catechol (CAT) is readily oxidized by silver ions followed by sulphanic acid (SA) nucleophilic attack. The resulting catechol derivative aggregates silver nanoparticles (Ag-NPs). The resulting product was characterized by different characterization techniques including UV-Vis spectrometry and transmission electron microscope (TEM). The SA-CAT induced aggregated Ag-NPs were used to develop a fast and ready to use colorimetric detection method for fluoride ion in water. In the presence of fluoride ions, the color of aggregated Ag-NPs solution changes from red to yellow with an absorbance decrease at 508 nm and an increase at 397 nm. Under the optimized conditions, the ratio of the absorbance intensity at 508 nm and 397 nm ( $A_{397}/A_{508}$ ) was proportional to the fluoride ion concentration in the range of 1-40  $\mu\text{M}$  with a detection limit of 0.2  $\mu\text{M}$ . The proposed new method was successfully used for the determination of fluoride concentration in the local spring water samples.

**Keywords:** Fluoride ion, Colorimetry, Ag-NPs, Nanosensor, Antiaggregation, Catechol, Sulphanilic acid

### **INTRODUCTION**

Fluoride ion with its unique chemical properties plays essential roles in many biological and biochemical environmental ecosystems as well as health care industries [1]. Although fluoride is an essential element for growth and dental care, its over intake can result in mottling of teeth, skeletal fluorosis, stomach problems and kidney disorders [2,3]. While a fluoride concentration of 0.5 to 1.0 ppm is considered a beneficial limit in drinking water, most regulatory standards are set at 2 ppm for fluoride ion [4]. This thin beneficial margin of fluoride level in water demands for more precise water quality control systems and more delicate detection methods [5].

Currently, many analytical methods have been introduced for the determination of fluoride in different samples [6-10]. A literature survey showed that colorimetric

and fluorescent chemosensing are well adopted alternative to the other methods due several advantages such as high selectivity, quick detection and cost friendliness. In the developed fluoride colorimetric and fluorescent detection methods, the target anion participates in cation-ligand complexation reactions or in formation of strong hydrogen bonding induced  $\pi$ -electrons of neutral ligand [11].

In recent decades, metal nanoparticles (NPs) including gold nanoparticles (AuNPs) and silver nanoparticles (Ag-NPs) as well as their functionalized forms proved to be effective colorimetric sensors for detecting organic or inorganic compounds at low concentrations, due to their high extinction coefficients and the distance dependent optical properties. The fact lays in the aggregation extent of nanoparticles since their interparticle distances are in charge of color changes and UV-Vis spectral properties of their aqueous solutions [12].

Due to the easy modification of AuNPs surfaces with a large number of different compounds as well as sharp and

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intense color changes during aggregation process, more attention has been focused on the development of new AuNPs-based colorimeter sensors compared to AgNPs. To the best of our knowledge, there is no report for the Ag-NPs based fluoride colorimetric detection so far. However, there are several reports about the application of Ag-NPs for the colorimetric detection of sulfate [13], iodide [14] and phosphate [15] and application of Au-NPs for the determination of fluoride [16-18].

Almost all developed colorimetric applications of silver nanoparticles are based on aggregation, whose most crucial challenge is the lack of stability and selectivity because many other external factors can also induce the aggregation of metal NPs [19]. Different modifiers have been used to enhance the selectivity behavior of AgNPs. Whether being stable or not, preparation of these compounds requires a long time, tedious preparation procedure and high costs [20]. In contrast, the anti-aggregation based colorimetric strategy may improve the selectivity owing to the lower possibility of false positive results.

In the current study, catechol (CAT), as a widely used precursor in pharmaceutical synthesis [21], is oxidized with silver ions to a preferred target for sulfanilic acid (SA) nucleophilic attack [22]. The synthesized SA-CAT derivative was used to prepare modified silver nanoparticles (SA-CAT-Ag-NPs). This novel compound was employed as a selective colorimetric reagent for fluoride ion detection based on anti-aggregation of Ag-NPs. The aggregation of AgNPs is readily inhibited by fluoride ions, leading to a color change from brown to yellow. The possible mechanism has been proposed based on the experimental results and literature. The proposed method was successfully applied for the colorimetric detection of the fluoride in local water springs. The results confirmed that the developed method is not only sensitive and selective for colorimetric detection of fluoride in water but also proved to be quantitative, simple and cost-effective in comparison to literature.

## EXPERIMENTAL

### Reagents and materials

All chemicals used were of analytical grade or the highest purity available. Silver nitrate ( $\text{AgNO}_3$ , 99.8%) was

purchased from Merck (Darmstadt, Germany). 1,2-Dihydroxybenzene (Catechol), >99% was purchased from Acros Organics (Fair Lawn, NJ). p-Aminobenzenesulfonic acid was obtained from Sigma Aldrich (Milwaukee, WI). All reagents were used without further purification. Ultrapure water was prepared by using a Milli-Q water purification system (Millipore, Bedford, MA). The stock solutions were prepared daily with ultrapure water. All experiments were carried out at room temperature. All glassware were thoroughly cleaned with freshly prepared 3:1 HCl/ $\text{HNO}_3$  solution and rinsed fully with deionized water before use.

### Instruments

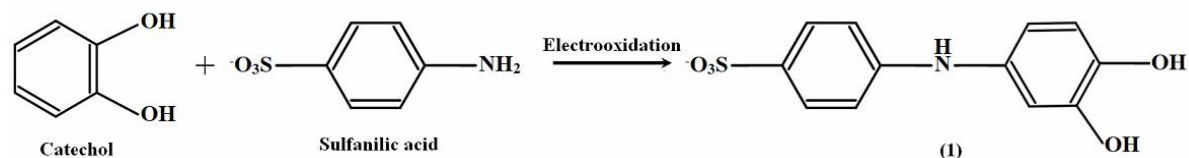
Changes in UV-Vis absorption spectra were monitored using a double-beam T80 + UV-Vis spectrophotometer PG (China) with a 1 cm quartz cell. For each measurement, 2 ml SA-CAT-AgNPs solution was used. TEM images were recorded by Philips CM30 Transmission Electron Microscopy right before and after the addition of fluoride to nanoparticle solutions. A Metrohm 827 pH meter equipped with a double junction glass pH electrode was used to control the pH of solutions. Potentiometric determination of fluoride was carried out using Metrohm pH/ion meter (Switzerland) equipped with fluoride ion selective electrode and Ag/AgCl-KCl reference electrodes.

### Preparation of SA-CAT-AgNPs

For the synthesis of SA-CAT-Ag-NPs, 20 ml of CAT (0.01 M) and 20 mL of SA (0.01 M) solutions were mixed via stirring for 15 min. Then, 10 ml  $\text{AgNO}_3$  (0.01 M) was added dropwise into mixture by stirring for another 20 min at room temperature. The resulting solution was stored away from light for 24 h before use in colorimetric measurements.

### Colorimetric Detection of Fluoride

The colorimetric detection of fluoride was performed at room temperature. For this purpose, various microliter volumes of 1 mM fluoride solution were added to 2 ml of the prepared SA-CAT-AgNPs solution probe and UV-Vis spectra were recorded after 2 min. To evaluate the probable interferences, the effects of various ions on the color change was investigated by the addition of 20  $\mu\text{l}$  of 1 mM of



Scheme 1

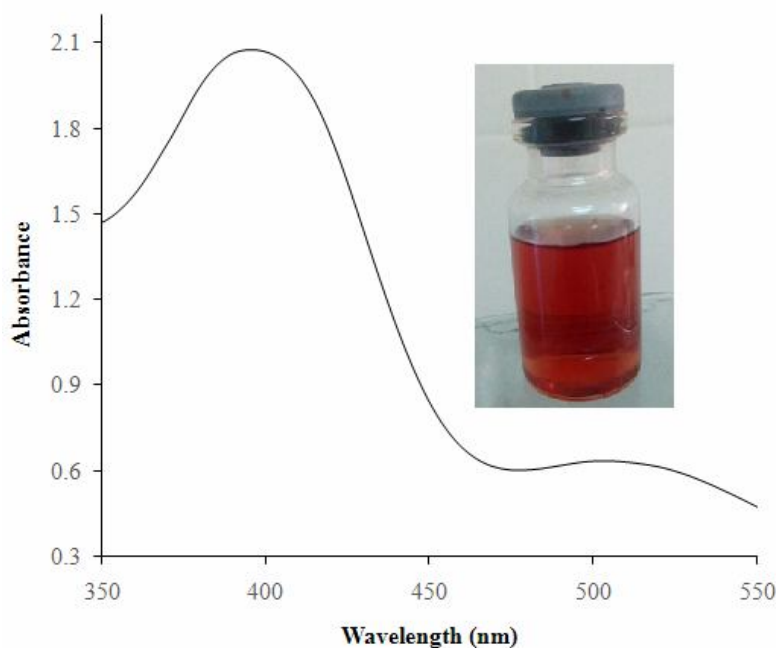


Fig. 1. UV-Vis absorption spectrum of synthesized SA-CAT-AgNPs and its corresponding photographic image.

various ions, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , into the 2 ml of SA-CAT-AgNPs solution.

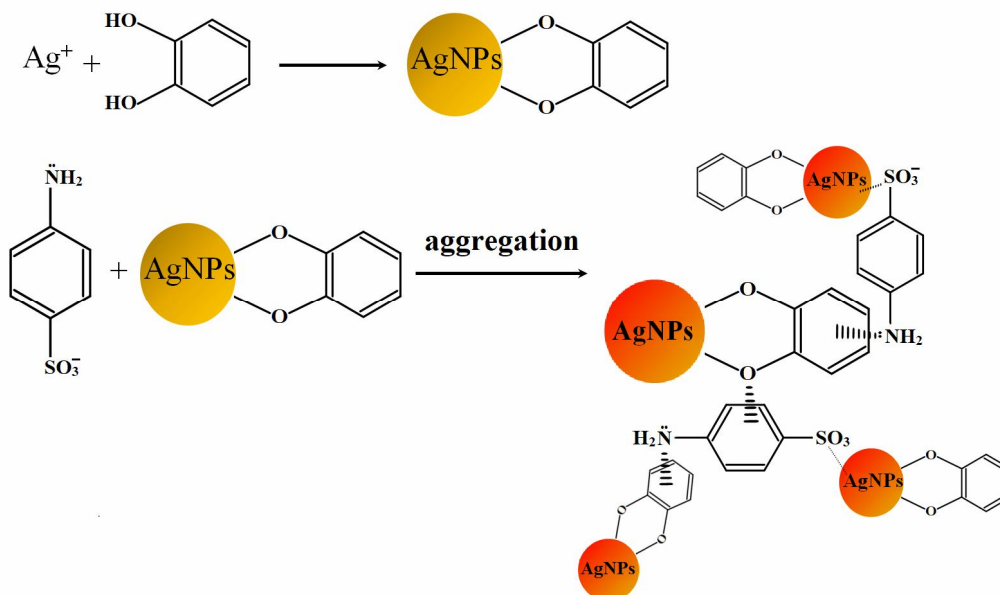
## RESULTS AND DISCUSSION

### Chemical Oxidation of CAT in the Presence of SA and Silver Ions

The electrochemical oxidation of CAT in the presence of various nucleophiles to synthesis different derivatives of catechol have been widely investigated [22-24]. In all reports, it was well known that CAT is oxidized to a very reactive intermediate o-benzoquinone which can be easily attacked by a nucleophile according to 1,4-(Michael) addition reaction. Accordingly, Nematollahi *et al.*

investigated the electrooxidation of CAT in the presence of SA and confirmed that the main product of this coupling reaction is (1), as the following reaction (Scheme 1) [22]:

This reaction motivated us to develop a new procedure for the preparation of functionalized silver nanoparticles as SA-CAT-AgNPs. To do so, silver ions were used for the chemical oxidation of CAT in the presence of SA as a nucleophile. In fact, we used CAT as reducing agent in preparation of silver atoms and the insitu formation of SA-CAT (product 1) to prepare modified silver nanoparticles. Figure 1 shows the UV-Vis spectra of solution containing silver ions, CAT and SA. As seen, a familiar surface plasmon resonance (SPR) band at 397 nm confirms the formation of silver nanoparticles in solution [25]. Another broad peak with low intensity at 510 nm as well as red



Scheme 2

color of obtained solution (inset of Fig. 1) shows the existence of aggregated silver nanoparticles in solution. This claim is fully supported by the result of TEM image. Figure 2a shows the TEM image of synthesized AgNPs using CAT and SA. As can be seen, a huge aggregation of nanoparticles has occurred during the reaction between reactants at this condition. Gebru *et al.* have reported the preparation of CAT capped silver nanoparticles [26]. Based on their results, CAT acts as a reducing as well as a stabilizing agent from -OH moieties. Moreover, the capping of silver nanoparticles with SA from  $-\text{SO}_3^-$  moiety has been reported by Huang *et al.* [27]. So, based on the electrochemical reaction between CAT and SA, literature reports and the our obtained results from UV-Vis spectrum of  $\text{CAT} + \text{SA} + \text{Ag}^+$ , the possible reaction pathway can be summarized as follows (Scheme 2).

According to scheme 2, silver ions oxidize the CAT molecules producing CAT-AgNPs for SA nucleophilic attack and aggregating silver nanoparticles to SA-CAT-AgNPs. Therefore, SA molecules probably attach to CAT and silver nanoparticles from  $-\text{NH}_2$  and  $-\text{SO}_3^-$  moieties, respectively.

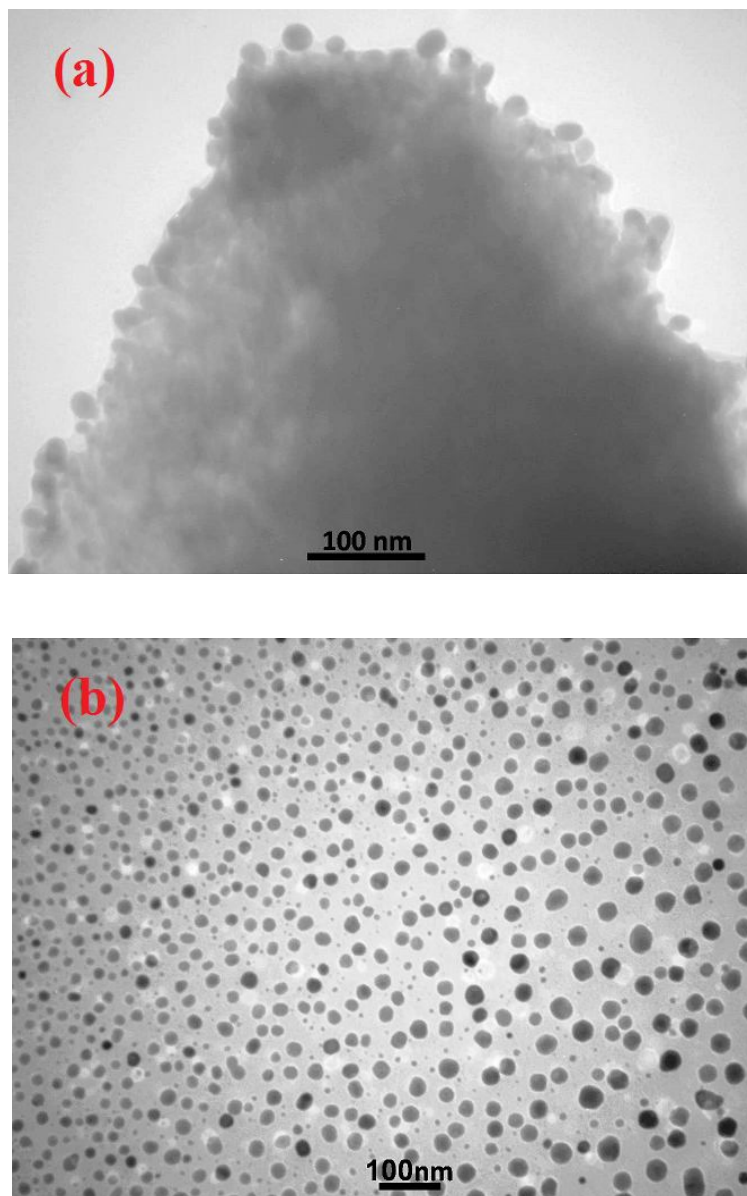
In the preparation of SA-CAT-AgNPs, the effect of CAT, SA and silver ion concentration and their sequence

addition to reaction mixture were evaluated. The optimum conditions were mixing of SA and CAT in first step and addition of silver ions to this mixture after 15 min in next stage (data not shown)(please see experimental section).

### Interaction between SA-CAT-AgNPs and Fluoride Ions

High negative charge density of fluoride ion and its high tendency for hydrogen bond formation are the principle of fluoride colorimetric and fluorimetric detection methods [11]. In more developed methods, fluoride ions adsorbed on positive sites *via* electrostatic attractions and/or acted as hydrogen bond acceptor. So, we investigated the interaction between fluoride ions with as-prepared SA-CAT-AgNPs due to partially positive charge of silver atoms and -NH group (as hydrogen bond donator) of substituted SA on CAT molecules.

Preliminary experiments showed that the color of SA-CAT-AgNPs solution changed from red to yellow after addition of fluoride ions. The UV-Vis spectra of SA-CAT-AgNPs and their images in the absence and presence of fluoride ions are shown in Fig. 3. As seen, fluoride ions induced the antiaggregation of SA-CAT-AgNPs and an increase and decrease (or completely disappearing) in SPR

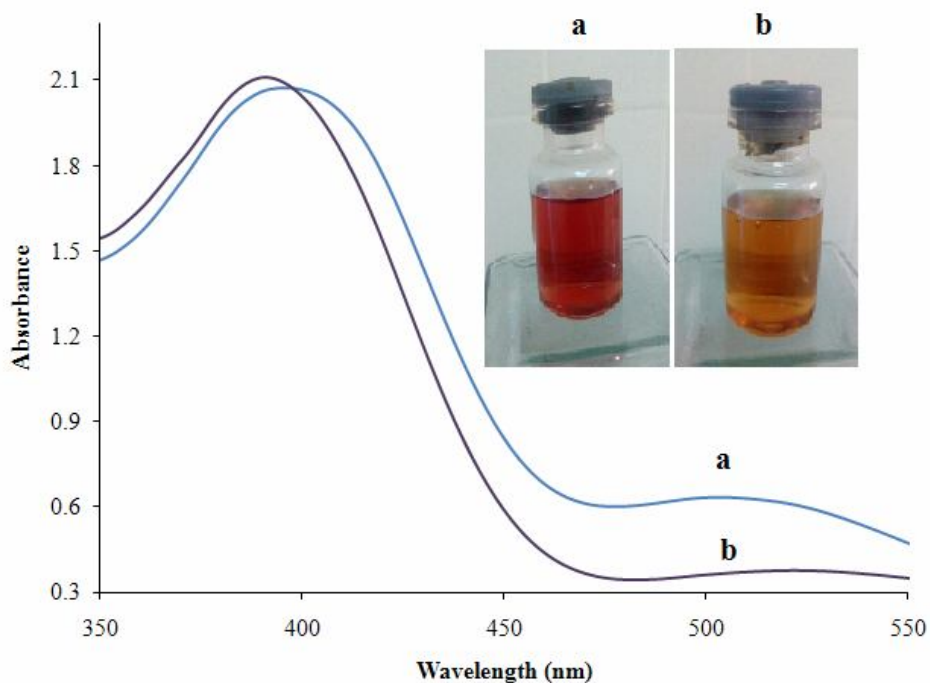


**Fig. 1.** TEM images of SA-CAT-AgNPs (a) before and (b) after the addition of fluoride ions.

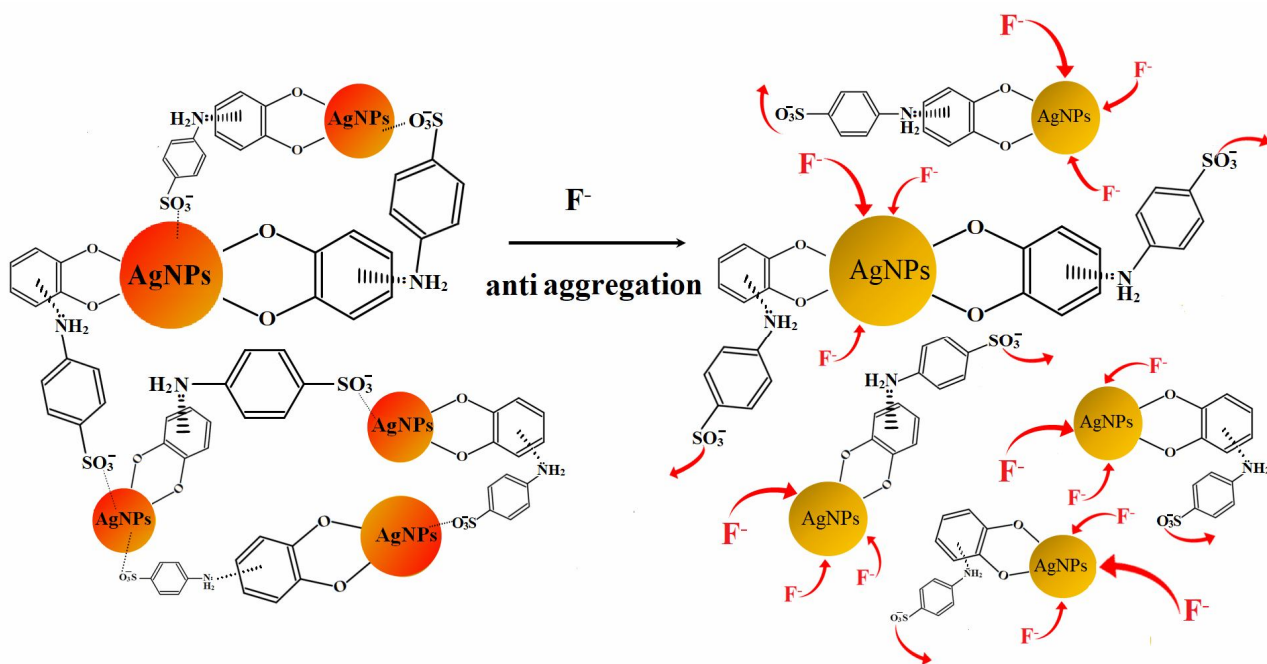
absorption intensity at 397 nm and 508 nm occurred, respectively. TEM image of SA-CAT-AgNPs after the addition of fluoride ions confirmed the antiaggregation of modified AgNPs (Fig. 2b). As can be seen from Fig. 2b, silver nanoparticles are completely separated and disaggregated after fluoride addition. Moreover, the color change from red to yellow accompanying to a blue shift of

SPR band of silver nanoparticles (about 20 nm) supported the antiaggregation process.

Figure 4 shows the proposed antiaggregation of SA-CAT-AgNPs after addition of fluoride ions. Accepting the proposed scenario, the antiaggregation of SA-CAT-Ag-NPs was induced through two different mechanisms; the cooperative adsorption of fluoride ions on the surface of



**Fig. 3.** UV-Vis absorption spectra of synthesized SA-CAT-AgNPs (a) before and (b) after the addition of fluoride ions, inset: The corresponding photographic images.



**Fig. 4.** The proposed mechanism for interaction of fluoride ions with aggregated SA-CAT-AgNPs.

silver nanoparticles and stripping the SA-CAT stabilizer from  $-\text{SO}_3^-$  moiety. However,

Contino *et al.* developed a colorimetric method for the selective determination of iodide ions based on tyrosine modified AgNPs [14]. According to their proposed mechanism sensing, iodide adsorption on silver nanoparticles was responsible for the stripping of tyrosine molecules from AgNPs. To verify our proposed pathway for fluoride sensing, the effect of iodide and chloride ions on UV-Vis spectrum of SA-CAT-AgNPs solution was also studied. The results showed that the antiaggregation of SA-CAT-AgNPs does not occur unless high concentrations of iodide and chloride ions are applied. These observations confirmed that the charge density of target anions plays an important role in the antiaggregation process and supported the possible adsorption of fluoride ions on silver nanoparticles which allowed the colorimetric detection of fluoride in aqueous solutions.

### Colorimetric Detection of Fluoride

In order to obtain the optimum conditions for the detection of fluoride, the effective parameters on  $A_{397}/A_{508}$  ratio in the antiaggregation process of SA-CAT-Ag-NPs were studied. As the most effective parameter, the solution pH was adjusted in the absence (blank) and presence of fluoride (25  $\mu\text{M}$ ) in the range of 2-11. The higher values of  $A_{397}/A_{508}$  indicated the higher degree of antiaggregation. Figure 5 shows the changes of  $A_{397}/A_{508}$  values versus solution pH. As can be seen, the value of  $A_{397}/A_{508}$  increases with increasing pH and then fixed between 4-9. The significant diminish of  $A_{397}/A_{508}$  and decrease in antiaggregation process at pHs  $< 4$  is probably related to formation of HF ( $\text{pK}_a = 3.2$ ). In this pH range, the preferred specie of fluoride is HF and there is not enough fluoride ion left for stripping SA-CAT from Ag-NPs. The considerable decrease in the values of  $A_{397}/A_{508}$  at pHs  $> 9$  is related to the antiaggregation of SA-CAT-AgNPs by  $\text{OH}^-$  ions in the absence of fluoride ions (blank solution). This phenomena is completely supported by the preparation of catechol stabilized Ag-NPs at alkaline media [26]. Since the solution pH of prepared probe was about 4.5 and the values of  $A_{397}/A_{508}$  were leveled off between pH = 4-9, there is no need for pH adjustment in determination of fluoride based

on the antiaggregation of SA-CAT-AgNPs. It must be noted that due to use of microliter volume of fluoride sample solution in the proposed procedure, the changes of pH during the addition of water sample to probe is very negligible and there is no need for buffers to fix the solution pH in detection system.

The optimum response time of the proposed probe to  $\text{F}^-$  was determined by monitoring the UV-Vis absorption spectra of 2 ml probe solution containing 25  $\mu\text{M}$  fluoride over the time periods of 1, 3, 5, 8, 10, 30 and 60 min. The changes of  $A_{397}/A_{508}$  values were reached to the maximum value after 1 min (data not shown), so, there is no limit for reaction time selection in the developed detection method.

To determine the quantitative characteristics of the fluoride colorimetric detection method, various microliter volumes of fluoride solution (0.1 mM) were added to 2 ml of SA-CAT-Ag-NPs solution and the changes of  $A_{397}/A_{508}$  was monitored. Figure 6 shows the obtained UV-Vis spectra and the corresponding calibration curve. The value of  $\Delta A = A_i - A_0$  ( $A_i$  and  $A_0$  are  $A_{397}/A_{508}$  ratio in the presence and absence of fluoride ion) increases with increasing the concentration of fluoride ion. The ratio was linearly proportional to the concentration of fluoride ( $R^2 = 0.9945$ ) from 1  $\mu\text{M}$  to 40  $\mu\text{M}$  (inset of Fig. 6). The detection limit of the proposed method was calculated to be 0.2  $\mu\text{M}$  for fluoride ion based on  $3 \times (S_b/a)$ .

The selectivity of the proposed method was investigated by monitoring the changes of  $A_{397}/A_{508}$  values in the presence of 40  $\mu\text{M}$  (equivalent to  $\text{F}^-$ ) of some ordinarily existing significant ions in water samples (Fig. 7). As can be seen from Fig. 7, the  $A_{397}/A_{508}$  values were not significantly different from that of standard fluoride solution. This interesting behavior is probably related to the high adsorption tendency of fluoride ions to silver nanoparticles.

A comparison of the proposed method with previous reported colorimetric methods based on AuNPs (see Table 1) indicated that the analytical performance of the proposed method is comparable with other methods and in the cases of selectivity, simplicity, low cost, no necessities to optimization and a very short analysis time it is superior. The proposed colorimetric method can be used for the monitoring the fluoride amounts in water samples instead of tedious standard method.

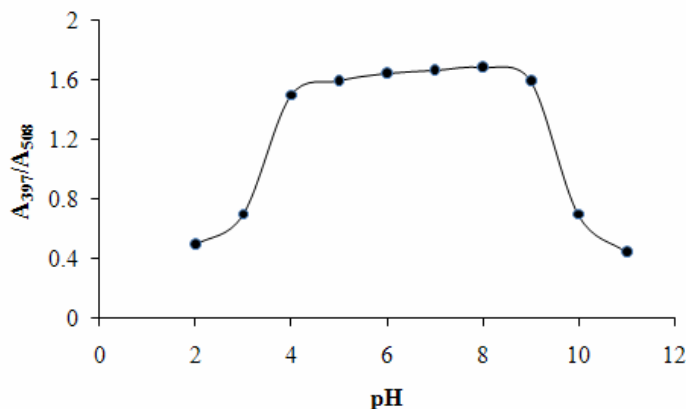


Fig. 5. The effect of solution pH on response of SA-CAT-AgNPs probe containing 25 μM fluoride.

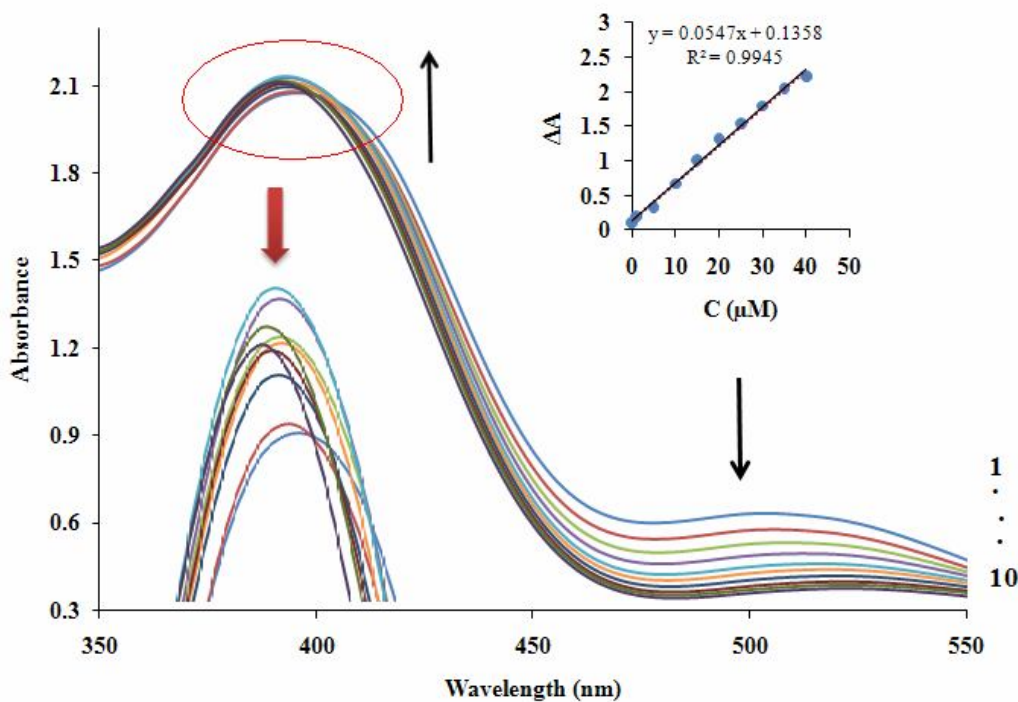


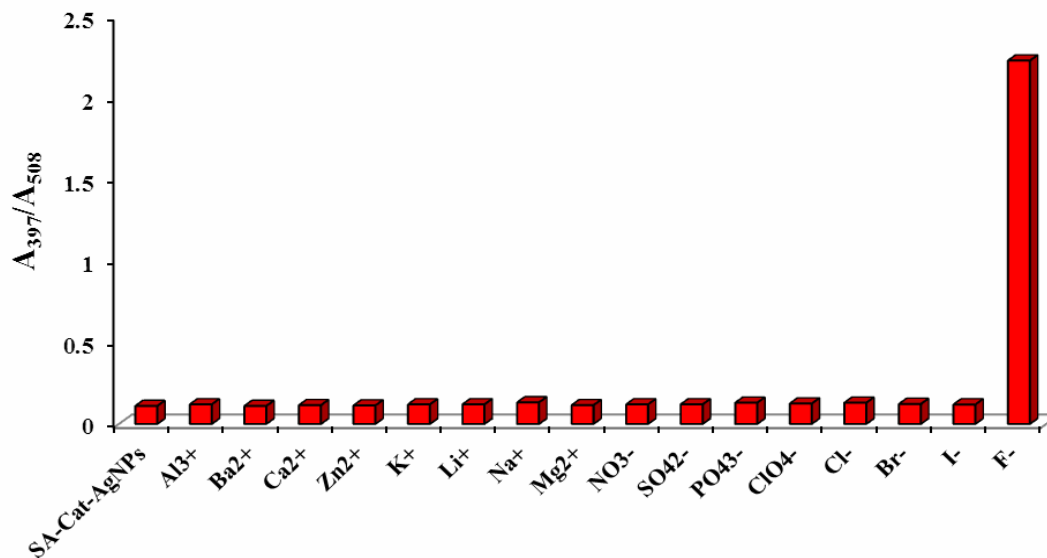
Fig. 6. UV-Vis spectra of 2 ml of SA-CAT-AgNPs solution containing (1) 0 and (2)-(10) 1- 40 μM fluoride, inset: The corresponding calibration curve as  $\Delta A = A_i - A_0$  ( $A_i$  and  $A_0$  are  $A_{397}/A_{508}$  ratio in the presence and absence of fluoride ion) vs. concentration of fluoride.

### The Assay of Fluoride in Real Samples

The proposed colorimetric method was applied to measure the amount of fluoride in springer water samples of Poldasht, Iran. For this purpose, 80 μl of water sample was

added to 2 ml of SA-CAT-Ag-NPs probe solution and the absorbance values were measured at 397 nm and 508 nm. The concentration of fluoride was determined by fitting  $A_{397}/A_{508}$  values on calibration curve. For a comparative





**Fig. 7.** The ratio of UV-Vis absorption intensity at 397 nm to absorption intensity at 508 nm ( $A_{397}/A_{508}$ ) for 2 ml SA-CAT-Ag NPs solution (blank) and blank containing 40  $\mu\text{M}$  of various ions.

**Table 1.** Comparison of the Analytical Characteristics of the Proposed Method with Previously Reported Colorimetric Methods Based on Nanoparticles for Detection of Fluoride

Ref.	LOD	LDR	Probe
[16]	23.7 $\mu\text{M}$	52-368 $\mu\text{M}$	Functionalized AuNPs
[17]	-	10-30 mM	Thioglucose-capped AuNPs
[18]	0.345 $\mu\text{M}$	10-30 $\mu\text{M}$	4-Mercaptophenylboronic modified AuNPs
This work	0.2 $\mu\text{M}$	1-40 $\mu\text{M}$	SA-CAT-AgNPs

**Table 2.** Determination of Fluoride in Springs Water (Poldasht, Iran)

Sample	Proposed method ( $\mu\text{g ml}^{-1}$ ) $\pm$ SD <sup>a</sup>	Standard method ( $\mu\text{g ml}^{-1}$ ) $\pm$ SD
1	0.84 $\pm$ 0.05	0.83 $\pm$ 0.05
2	0.48 $\pm$ 0.02	0.47 $\pm$ 0.10
3	1.15 $\pm$ 0.05	1.16 $\pm$ 0.11
4	2.15 $\pm$ 0.10	2.17 $\pm$ 0.05

<sup>a</sup>Standard deviation (n = 3).

reference, the amount of fluoride in water sample was measured by potentiometric standard method [28]. The obtained results from sample analysis using proposed and standard methods are summarized in Table 2. The statistical t-test applied to the results showed no significance difference between fluoride average values obtained from proposed and standard methods. The results suggest that the proposed method has good analytical characteristics of fluoride detection in water samples.

## CONCLUSIONS

In summary, for the first time, this work presents development of a novel detection method for the colorimetric determination of fluoride based on nanoparticles. The proposed method is based on the antiaggregation of SA-CAT-AgNPs in the presence of fluoride ions. The addition of fluoride ions to SA-CAT-AgNPs solution resulted a blue shift in SPR band of silver nanoparticle and a simultaneous change in the color of the solution from brown to yellow. The absorbance intensity increases at 397 nm and decreases at 508 nm. The antiaggregation process is probably due to adsorption of fluoride (with high charge density) on silver atoms and release of capping agent from  $-\text{SO}_3^-$  moiety. The changes of  $\Delta A$  values in UV-Vis spectra are linearly proportional to fluoride ions concentration in the range of 1-40  $\mu\text{M}$  with a coefficient of determination of 0.9945. No need for pH adjustment, high sensitivity and acceptable selectivity, simplicity and rapid reaction type are the unique characteristics of the proposed fluoride colorimetric detection method. The method can be reliably used for the determination of fluoride in water samples in aqueous media.

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