



Colorimetric Detection of Iron(III) Ion Based on 4-Aminothiophenol and Schiff Base Naphthalene-2-ol Modified Silver Nanoparticles

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A facile, highly selective colorimetric sensor based on 4-aminothiophenol (4-ATP) and Schiff base naphthalene-2-ol (L) modified silver nanoparticles (4-ATP-L-AgNPs) for detection of Fe(III) ion in aqueous solution. The presence of Fe(III) ion induced the aggregation of AgNPs that caused the red-shift from 430 to 440 nm, through a cooperative metal-ligand interaction from the coordination bond between Fe(III) ion and functional groups on AgNPs surface resulting in a colour change from dark brown to dark yellow with increasing absorption at 365 nm. The absorbance at 365 nm is linear with the concentration of Fe(III) ion ranging from 9.0×10^{-6} M to 9.0×10^{-3} M with a correlation coefficient of 0.9991. The detection limit of the developed method was 7.9×10^{-6} M. The practical application of 4-ATP-L-AgNPs for selective sensor for Fe(III) ion in various drinking water samples were demonstrated.

Keywords: Colorimetric detection, Modified silver nanoparticles, Iron(III) ion, Water samples.

INTRODUCTION

It is well known that iron is the highest transition metal in the cellular system [1]. As crucial elements in living organisms, many proteins use iron for oxygen transport, electron transport, and as a catalyst in oxidoreductase reactions [2]. Deficiency or overloading of iron can induce various biological disorders in the living body, such as anemia, liver and kidney damage, diabetes and heart failure [3]. According to Public Health Service, the tolerance limit of iron is 0.3 mg/L for public water supplies. Therefore, the detection of iron in water is important to monitor the quantity of iron in the environment at safe levels.

Ordinarily, various analytical techniques including atomic absorption spectroscopy (AAS) [4], inductively couple plasma mass spectrometry (ICP-MS) [5,6], mass spectrometry (MS) [7], fluorescence spectroscopic analysis [8], *etc.* for the iron determination has been reported in the literature. Most of these techniques involve tedious, complex procedures, and are time-consuming, which makes them inconvenient.

Colorimetric sensors have shown in analyses to be simple and convenient for the determination of iron(III) ion and can be applied to the sample source [9-12]. However, some disadvantages are associated with these sensors in the synthesis and

applications including the cumbersome multi-step processes, use of harmful organic solvents and having a low yield. In addition, most colorimetric sensors are insoluble in water rendering them less useful in real sample analysis. Among colorimetric sensors, metal nanoparticles have been widely used as colorimetric sensors for the chemical sensing of various metal ions [13]. Silver nanoparticles (AgNPs) colorimetric sensors have many advantages over gold nanoparticles, such as having higher extinction coefficients and lower prices, thus allowing detection with minimal material consumption [14]. The methods of determination rely on the colour changes associated with the surface plasmon resonance, which are dependent on their size and shape of nanoparticles [15]. Additionally, they have an important role to develop metal nanoparticles as chromogenic sensors for metal ions through surface modification of metal nanoparticles. For example, the use of a stabilizing agent, such as small organic ligand or biomolecules, which links AgNPs together through metal-ligand interaction, provides the stability of nanoparticles as well as the desired selective chromogenic sensing of various heavy metal ions [16,17].

Surface modification of AgNPs with a co-stabilizing agent is of great interest owing to increase in their selectivity property [18]. The synthesis of L-AgNPs has been reported earlier by

our group [19]. The interference studies revealed a high selectivity to iron(II) and iron(III) ions over a series of other cations, and this method has been effectively applied for the determination of iron(II) ion in multivitamin tablet samples. In this article, a simple and rapid chromogenic sensors is developed for iron(III) ion using silver nanoparticles, which were modified with Schiff base naphthalene-2-ol (L) in conjunction with 4-aminothiophenol. Both stabilizing agents contain various functional groups, which can be easily adsorbed onto the surface of silver nanoparticles and increase selectivity for binding with iron(III) ion. This probe was successfully developed to detect iron(III) ion in three source types of drinking water samples.

EXPERIMENTAL

All the reagents and solvents were of analytical grade and used without further purification. Standard stock solution of metal ions (Zn^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Fe^{2+} and Fe^{3+}) were prepared with deionized water (0.1000 M) from their perchlorate salts. 2-Hydroxy-1-naphthaldehyde, *m*-xylylenediamine and 4-aminothiophenol were purchased from Sigma-Aldrich Chemical Company and stored in desiccators containing self-indicating silica. The UV-Vis spectroscopic experiments were performed on a Shimadzu UV-Vis 2401PC spectrophotometer. The size and morphology of synthesized AgNPs were examined by using a Philips Tecnai F20 G2 transmission electron microscope (TEM) operated at 120 kV.

Synthesis and characterization of AgNPs modified by Schiff base naphthalene-2-ol (L) and 4-aminothiophenol (4-ATP): Silver nanoparticles were synthesized through a simple and rapid chemical reduction method. Firstly, ligand and 4-ATP solutions in ethanol (12.5 mL of 5×10^{-4} mol L^{-1}) with 0.003 g of NaBH_4 were mixed under vigorous magnetic stirring at 78 °C for 30 min. After that silver nitrate solution (25 mL of 5×10^{-4} mol L^{-1}) was added into the mixed solution under constant stirring after half an hour at 78 °C. The dark brown solution indicated a reduction of silver ions into AgNPs and showed strong characteristic SPR around 430 nm. All procedures were repeated at least three times to confirm the reproducibility and the modified AgNPs was carried out after allowing

the solution to stand at room temperature for more than one week. The size and morphology of ligand and 4-ATP modified AgNPs were characterized by using high resolution transmission electron microscopy and UV-vis spectrometry.

RESULTS AND DISCUSSION

Characterization of 4-ATP-L-AgNPs: Schiff base naphthalene-2-ol (L) was synthesized with a high yield (82 %) [19]. The ligand molecule was able to be used as a co-stabilizing agent with 4-ATP to produce 4-ATP-L-AgNPs in aqueous solution with a dark brown colour. The UV-visible absorption studies of 4-ATP-L-AgNPs showed the maximum wavelength at 430 nm (Fig. 1a). The size and morphology of samples were examined using HR-TEM, which exhibited the formation of spherical crystalline dispersed AgNPs with the average size of approximately 15.07 nm (Fig. 1b). It can be seen in Fig. 1b that silver nanoparticles exhibited a spherical shape with uniform particle size. Fig. 1b inset shows the magnified HRTEM image of a silver nanoparticles. The lattice fringe space was measured to be 0.23 nm which corresponds to Ag (111).

Selection of iron(III) ion using 4-ATP-L-AgNPs: The chromogenic sensing properties of 4-ATP-L-AgNPs for a series of transition metal ions including Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} were explored in aqueous solution. The results in Fig. 2a illustrate that modified AgNPs showed a change in colour upon the addition of Fe(III) ion from dark brown to yellow while the addition of Fe(II) ion resulted in only a slight change of colour. Meanwhile, the addition of other metal ions did not exhibit any significant colour change. Moreover, modified AgNPs was carried out by UV-visible spectroscopy. The results indicated that modified AgNPs showed high selectivity for iron(III) ion with a significant increase in the absorption band from 300 to 380 nm according to ligand-to-metal charge-transfer (LMCT) (Fig. 2b). As one can observed, the absorption of iron(III) ion increased more than iron(II) ions, and thereby suggests that Fe(III) ion is the most selective for 4-ATP-L-AgNPs. Therefore, interaction between 4-ATP-L-AgNPs and Fe(III) ion was examined using UV-Vis spectroscopic titration data with the addition of different volumes of 10^{-2} mol L^{-1} Fe(III) ion into AgNPs solution (Fig. 3a). The

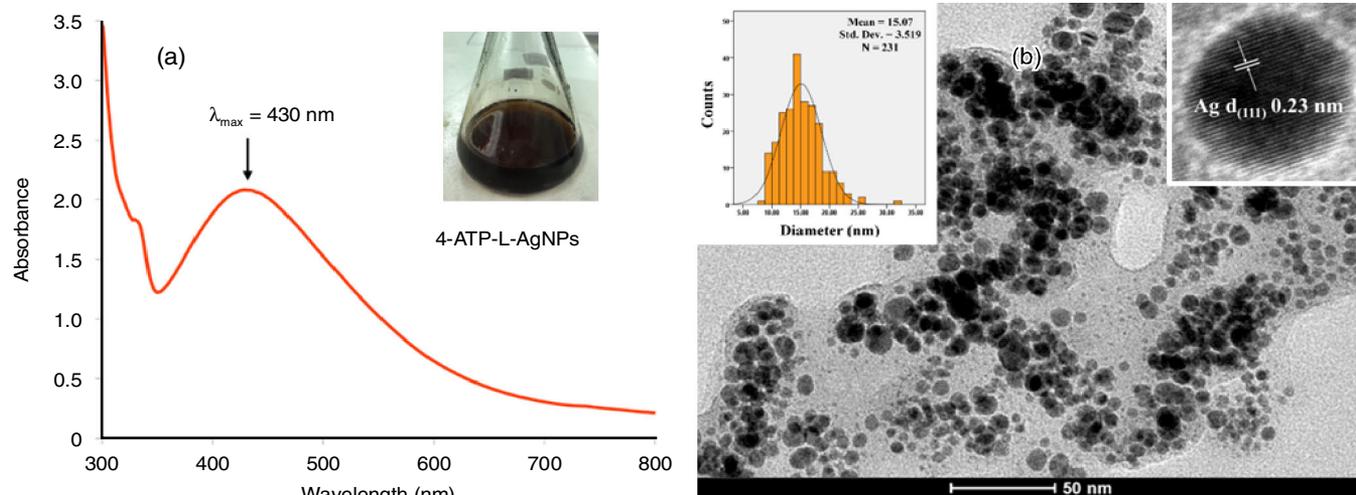


Fig. 1. UV-visible absorption spectrum (a) and HR-TEM image (b) of 4-ATP-L-AgNPs

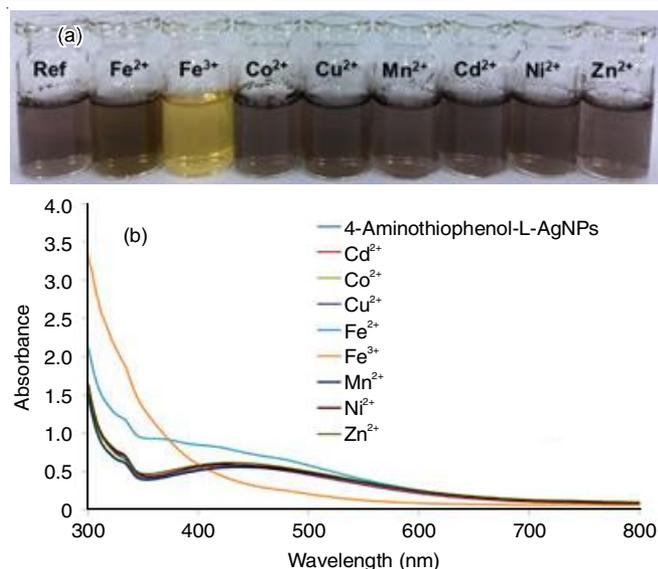


Fig. 2. Digital images (a) and absorption spectra of 4-ATP-L-AgNPs (b) with various transition metal ions

results found that the absorbance of 365 nm increased in a linear fashion with a concentration of Fe(III) ion. In addition, an increase of Fe(III) ion concentration would induce a decrease in AgNPs' maximal absorption at 430 nm accompanying an obvious enhancement of new peak at 440 nm due to the presence of Fe(III) ion induced the aggregation of 4-ATP-L-AgNPs in relation (Fig. 3a). The absorbance of 365 nm having concentration of Fe(III) ion in the range of 9.0×10^{-6} M to 9.0×10^{-3} M also showed a good linear relationship with a correlation coefficient of 0.9991 (Fig. 3b). The limits of detection (LOD) for Fe(III) ion was found to be 7.9×10^{-6} M. These results indicated that 4-ATP-L-AgNPs can be used as highly selective and sensitive colorimetric sensors for the detection of Fe(III) ion.

Sensing mechanism: The aggregation characteristic of AgNPs depends on the concentration of metal ion and binding of functional groups on the nanoparticles surface [20]. 4-ATP-L-AgNPs are induced to aggregate by adding Fe(III) ion through the formation of 4-ATP-L-AgNPs and Fe(III) complex; thus, a possible mechanism for the chemosensor of Fe(III) ion is proposed (Fig. 4).

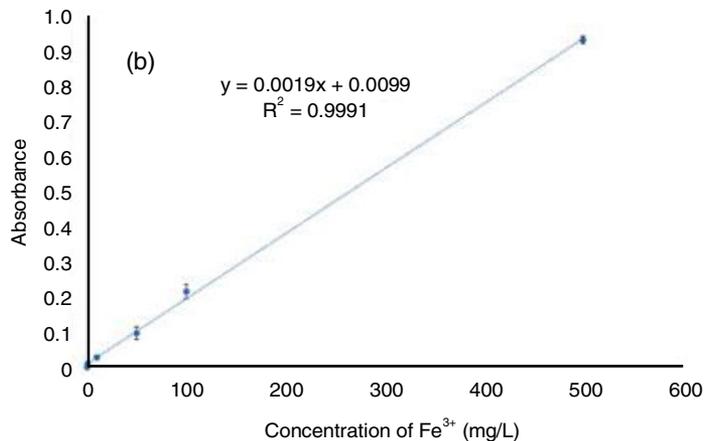
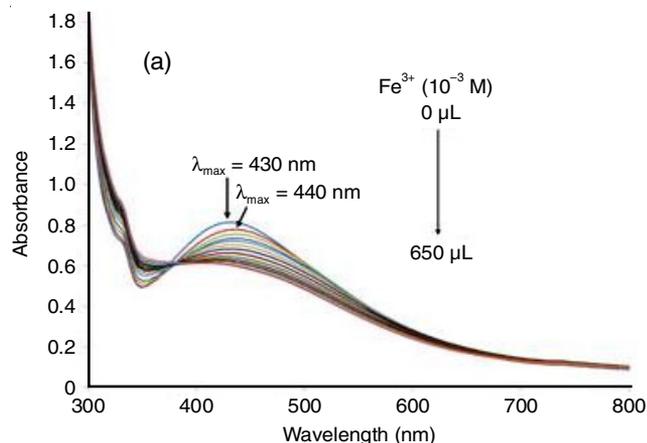


Fig. 3. UV-visible titration results of 4-ATP-L-AgNPs with increasing volume (0-650 mL) of 10^{-2} mol L $^{-1}$ iron(III) ion (a) and linear relationship between absorption intensity change of L modified AgNPs and concentrations of iron(III) ion ranging from 9.0×10^{-6} M to 9.0×10^{-3} M (b)

A SPR band in 4-ATP-L-AgNPs red-shift from 430 to 440 nm and decrease when increasing the Fe(III) ion. A comparison of TEM images between 4-ATP-L-AgNPs (Fig. 5a) and 4-ATP-L-AgNPs with Fe(III) ion (Fig. 5b) shows a significant difference in size and morphology. 4-ATP-L-AgNPs are dispersed into a spherical crystalline with average size of 15.07 nm, but 4-ATP-L-AgNPs with Fe(III) ion coagulated together to a bulky cluster with the addition of Fe(III) ion. Additionally, an absorbance of 365 nm increased in good linearity with a concentration of Fe(III) ion with the ligand-to-metal charge-transfer (LMCT) from a strong interaction of functional groups on AgNPs surface (-OH and -NH₃ group), and their ligand molecular orbital charge transfers to *d*-orbitals of Fe(III) ion. This results in intense absorption bands that show a dark yellow solution. Both results suggest that Fe(III) ion intensely induces the aggregation of 4-ATP-L-AgNPs.

Interference studies: In order to explore the selectivity of 4-ATP-L-AgNPs, the effects of other cation species on the binding with 4-ATP-L-AgNPs were carried out. The experiments were performed by adding different concentrations of potential interfering substances into 4-ATP-L-AgNPs containing iron (III) ion (0.001 mol L $^{-1}$) solution. As shown in Fig. 6, the UV-visible absorption spectra of 4-ATP-L-AgNPs complex at 430 nm were not influenced by foreign cations (absorption change intensity less than 2.5 %). As illustrated in Table-1, the relative error of common interference transitional metal ions, which can regarded as acceptable means that 4-ATP-L-AgNPs would be used for the detection of Fe(III) ion in drinking water samples.

TABLE-1
INTERFERENCE OF OTHER METAL IONS ON THE
UV-VISIBLE SPECTROSCOPY DETERMINATION OF Fe $^{3+}$

Interference	Concentration ^a (M)	Absorbance $\Delta A = A - A_0$	Relative error (%) $(\Delta A/A_0) \times 100$
Cd $^{2+}$	1×10^{-2}	-0.0125	1.2481
Co $^{2+}$	1×10^{-2}	-0.0092	0.9193
Cu $^{2+}$	1×10^{-2}	-0.0186	1.8610
Fe $^{2+}$	1×10^{-2}	0.0046	0.4559
Mn $^{2+}$	1×10^{-2}	-0.0239	2.3916
Ni $^{2+}$	1×10^{-2}	-0.0055	0.5456
Zn $^{2+}$	1×10^{-2}	0.0253	2.5336

^aRefers to the concentration of Fe $^{2+}$ fixed at 1×10^{-3} M.

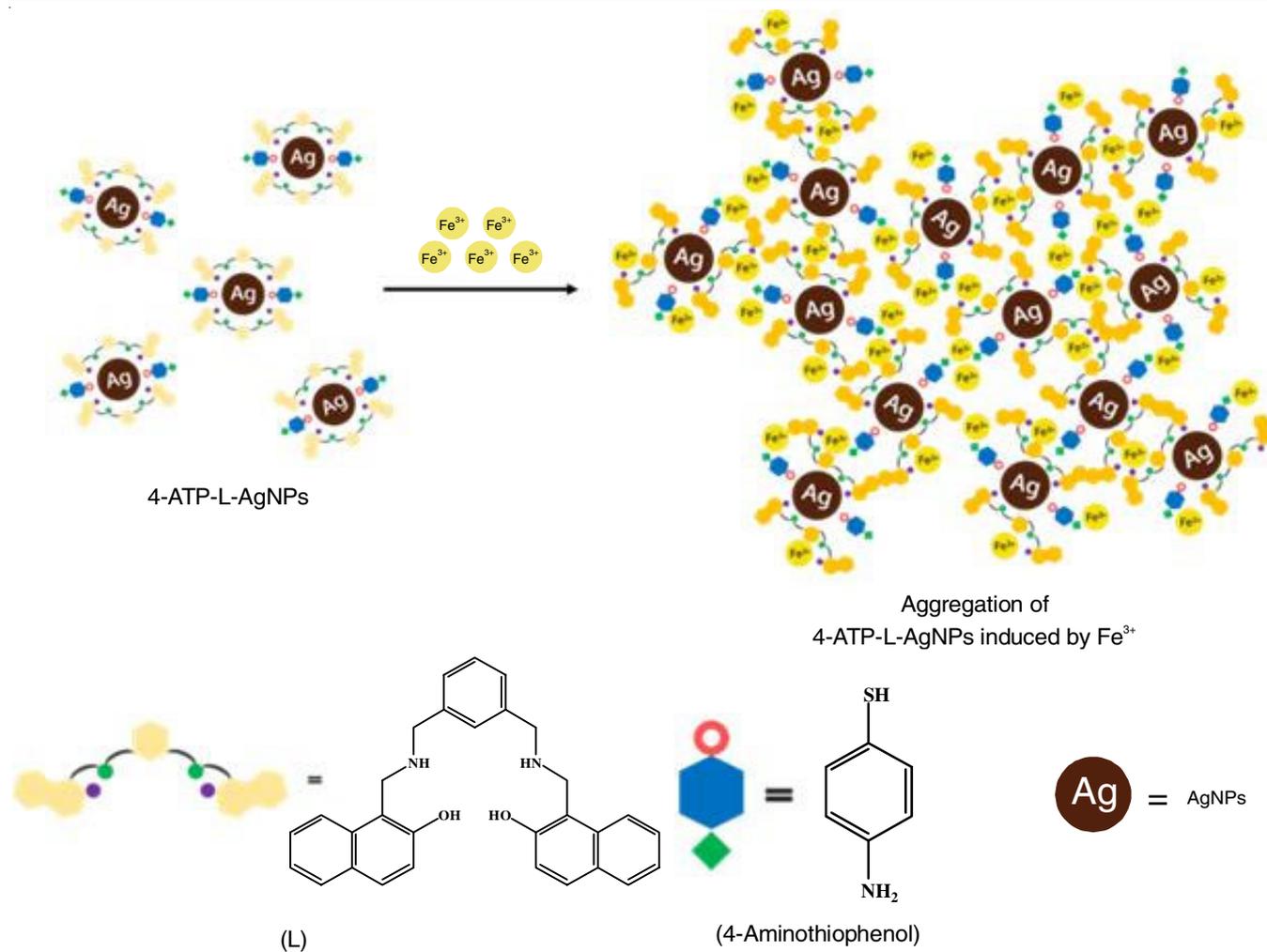


Fig. 4. Schematic illustration on the aggregation purpose mechanism of 4-ATP-L-AgNPs induced by iron(III) ion

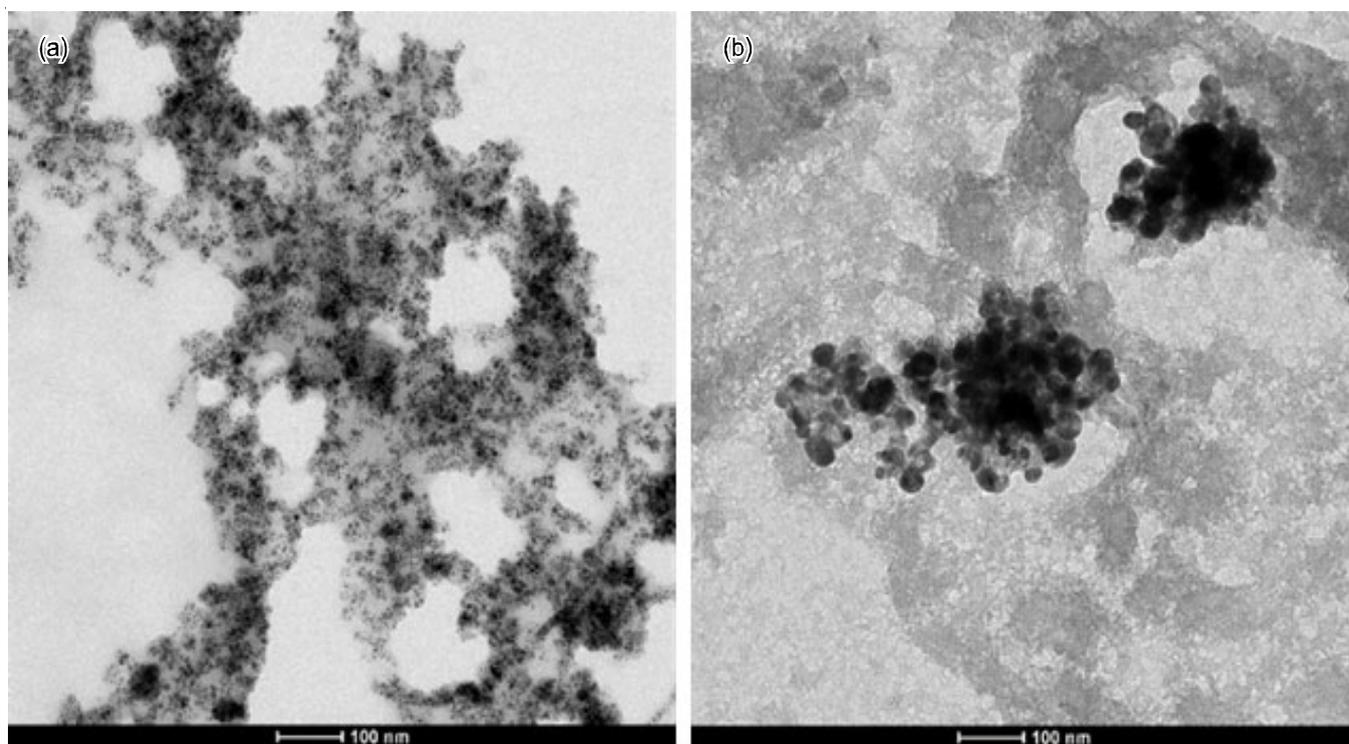


Fig. 5. HR-TEM images of iron(III) ion ion-induced 4-ATP-L-AgNPs aggregation

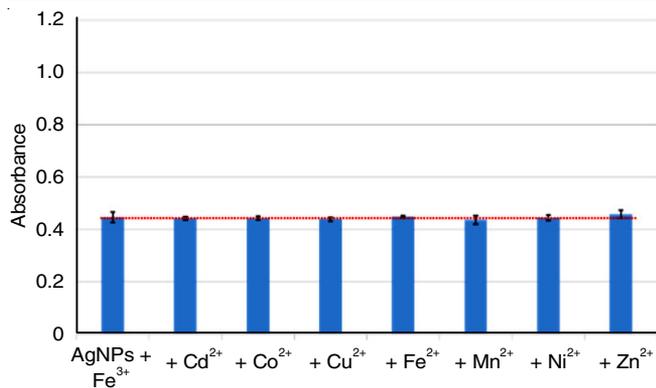


Fig. 6. Relative absorbance of 4-ATP-L-AgNPs at 365 nm in presence of various metal ions in aqueous solution

Application of 4-ATP-L-AgNPs for the detection of Fe(III) ion in drinking water samples: For investigation of potential of this developed approach, standard recovery experiments were performed in different drinking water samples (drinking, mineral and tap water) which were collected from different areas and of different brands. As shown in Table-2, the recoveries were 98.37-102.88 with a relative standard deviation (% RSD) < 2.47 % in three drinking water samples. These satisfactory results indicated that developed chemosensor 4-ATP-L-AgNPs method provides an accurate, precise results with no matrix effects in the real samples.

TABLE-2
ANALYSIS OF IRON(III) ION IN WATER SAMPLES
USING 4-ATP-L-AgNPs AS A SENSOR

Water samples (n = 3)	Concentration (mg/L)	Recovery ± SD
Drinking water	0.5	102.06 ± 2.47
	50	101.24 ± 0.96
	500	100.89 ± 0.72
Mineral water	0.5	102.88 ± 0.75
	50	102.57 ± 1.42
	500	99.42 ± 0.36
Tap water	0.5	98.37 ± 0.64
	50	101.90 ± 1.45
	500	100.33 ± 1.54

The performance of proposed chromogenic detection was compared with the previous studies of sensing probes for Fe(III) ion detections. As shown in Table-3, present 4-ATP-L-AgNPs sensing material offered a wide range of detection with low detection limit of 7.9 μM, and the colour change of the chromogenic approach was immediately observed with naked eye. Therefore, the system showed a potential to be applied as detection device for Fe(III) ion in natural water resources.

TABLE-3
PERFORMANCES COMPARISON OF DIFFERENT SENSORS FOR Fe³⁺ ION

Detection probe	Detection mechanism	Linear range	LOD	Ref.
Gold nanoparticles	Aggregation	10–60 μM	5.6 μM	[21]
Fuorophore	Coordination	0-100 μM	–	[22]
Chromophore	Coordination	0-100 μM	5.37 μM	[23]
Graphene quantum dots	Coordination	0-400 μM	7.22 μM	[24]
N-graphene quantum dots	Coordination	1-70 μM	0.08 μM	[25]
Metal organic framework (MIL-53)	Ions exchange	3-200 μM	9 μM	[26]
Silver nanoparticles	Reduction	0.08-80 μM	0.08 μM	[27]
Silver nanoparticles	Aggregation	9 μM -9 mM	7.9 μM	This work

Conclusion

A chromogenic detection of iron(III) ion using Schiff based naphthalene-2-ol (L) and 4-aminothiophenol (4-ATP) modified silver nanoparticles (4-ATP-L-AgNPs) was developed. The detection of iron(III) ion present in an aqueous solution was based on changes in absorbance resulting from ligand-to-metal charge-transfer which has a maximum absorption at 365 nm with concomitant naked eye color change from dark brown to dark yellow and the absorbance significantly shifted from 430 to 440 nm because the presence of iron (III) ion induced from the aggregation of 4-ATP-L-AgNPs. A linear calibration graph in the range of 9.0×10^{-6} mol L⁻¹ to 9.0×10^{-3} mol L⁻¹ Fe(III) ions with a detection limit of 0.44 mg/L was obtained. The sensing system successfully showed the potential application for colorimetric detection of Fe(III) ion in drinking water samples using the proposed surface-modified AgNPs with accurate results and rapid preparations.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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