A novel chemosensor for Ag(I) ion based on its inhibitory effect on the luminol–H₂O₂ chemiluminescence response improved by CoFe₂O₄ nano-particles

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**A B S T R A C T**

In the present study, we report on a simple, sensitive and selective chemosensor for the recognition and monitoring of silver ions in aqueous solutions. It is based on the inhibitory effect of Ag(I) ion on the chemiluminescence signal of H₂O₂–luminol system, which could be improved by at least 10-folds in the presence of cobalt ferrite (CoFe₂O₄) magnetic nano-particles. The structure and morphology of the synthesized CoFe₂O₄ nano-particles were characterized by X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy. The as-prepared CoFe₂O₄ nano-particles were then used as catalysts for H₂O₂–luminol chemiluminescence system. The enhanced chemiluminescence signal was dramatically decreased by adding trace levels of Ag(I) ion into the solution. The possible mechanism to explain this finding was discussed. Several parameters affecting the analytical signal such as the pH value, the concentrations of H₂O₂, luminol and CoFe₂O₄ nano-particles, incubation time and interfering ions were investigated and optimized. Under the optimized experimental conditions, chemiluminescence intensity of luminol–H₂O₂–CoFe₂O₄ versus Ag(I) concentration gave a linear response within the range of 0.5–100 ng mL⁻¹ with a detection limit of 0.15 ng mL⁻¹. The method was successfully applied to monitoring Ag(I) in various water samples.

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1. Introduction

Silver (Ag) has been recognized as a high demand metal due to its important roles in many aspects of human life. Silver compounds and alloys have widely been used as disinfectant and antibacterial reagents in wastewater treatment, dental and pharmaceutical preparations and food processing. On the other hand, silver at levels higher than needed can be harmful. Especially, long exposure to silver or its repeated intake may cause several health effects such as breathing problems, lung and throat irritation, stomach pain and pigmented disorders [1,2]. The United States Environmental Protection Agency (EPA) has established the maximum contaminant level for Ag in drinking water at 50 μg L⁻¹ [3]. Considering these facts, applying a simple, rapid and accurate method to monitor silver ion at trace levels in various samples is of great importance.

Various instrumental techniques including spectrophotometric methods [4,5], voltammetry [6,7], flame atomic absorption spectrometry [8,9], rayleigh light-scattering [10], spectrofluorometry [11,12], chemiluminescence [13], phosphorescence methods [14,15], inductively coupled plasma optical emission spectrometry [16], inductively coupled plasma mass spectroscopy [17,18] and ion exchange chromatography [19] have been developed for the determination of the silver ion. Most of these methods have important limitations and problems that are related to need a sample preparation system, time consuming, expensive and/or complicated analysis systems, boring and hard operation.

Magnetic nano-particles (MNPs) have been paid much attention in recent years due to their unique physical and chemical properties [20,21]. MNPs are advantageous for several analytical methods because they have a large surface-to-volume ratio, are comparable in size to many analytes of interest, are readily dispersible in solution, and have physical properties that are useful for enhancing signal detection. Emerging analytical techniques and new uses of conventional methods have begun to integrate MNPs to take advantage of the ability to magnetically induce motion, enhance signals, and switch behaviors. Although MNPs have been used in various analytical methodologies such as (a) pre-concentration, separation, and capture of analytes; (b) sensors and detection; and (c) imaging, to date, most of the investigations on MNPs were
concerned with their separating ability and some of these applications were summarized in recently published review articles [22–24]. In 2007, Gao and co-workers reported that MNPs possess an intrinsic enzyme mimetic activity similar to that found in natural peroxidases, though MNPs are usually thought to be biological and chemical inert [25]. MNPs as peroxidase mimetic could catalyze luminol oxidation by H2O2 to produce intensified chemiluminescence (CL). Because of weak selectivity, the limited studies have been reported for analytical application of MNPs amplified CL system [26–31], and it remains a challenge to achieve the selectivity in direct CL detections while improving CL efficiency.

In this work, we report on a novel concept of developing intrinsically selective CL switching at the surface of CoFe2O4 MNPs for the sensitive detection of Ag(I) ion. The decomposition of H2O2 to generate superoxide anions and hydroxyl radicals could be catalyzed at the surface of CoFe2O4 MNPs, improving the CL signal of H2O2–luminol system by at least 10-folds. However, in the presence of silver nitrate, Ag(I) ions could be reduced to Ag atoms by luminol, covering instantly the surface of CoFe2O4 MNPs. Consequently, the catalyzed process of the present CL reaction is effectively inhibited through the surface covering of CoFe2O4 MNPs with Ag atoms, leading to a decreased CL signal. This reduction is directly dependent on the Ag(I) concentration, so that, the CL intensity is gradually decreased with the increase in Ag(I) concentration. To the best of our knowledge, this is the first time that the MNPs intensified CL system is used to determine trace levels of Ag(I) ions in aqueous solutions.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical-reagent grade. The high-purity deionized water (obtained from Ghazi Serum Co., Tabriz, Iran) was used throughout the experiment. All salts used for the interference study, silver nitrate (AgNO3) and sodium hydroxide (NaOH) were purchased from Merck (Darmstadt, Germany). Luminol and hydrogen peroxide (H2O2) were obtained from Acros organics (New Jersey, USA). A stock solution of 100 mg L−1 Ag(I) was prepared by dissolving proper amount AgNO3 in deionized water and stored in a dark place. The working solutions were prepared daily by diluting the stock solution. All the plastic and glassware used for the trace analysis were soaked in 15% nitric acid and cleaned before use.

2.2. Apparatus and instruments

Chemiluminescence spectra were recorded by FP-6200 spectrophotofluorometer (JASCO Corp., Tokyo, Japan) under the model of fluorescence scan with the excitation light source being turned off. The instrument is equipped with a 150 W xenon lamp, 1.0 cm quartz cell, dual monochromaters (silicon photodiode for excitation and photomultiplier for emission), Peltier thermostatted single cell holder model ETC-272 (JASCO Corp., Tokyo, Japan), and supported with PC-based Windows® Spectra Manager TM software for JASCO Corporation version 1.02. The slit width for emission is set at 20 nm and the CL spectra were recorded at a scan rate of 250 nm min−1. CL intensities were measured at 425 nm at 25 °C. The UV–vis absorbance spectra were recorded on a T80 (PG Instrument Ltd, England) spectrophotometer.

In order to identify the crystal structure of as-prepared nanoparticles, powder X-ray diffraction (XRD) measurements were performed by employing a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) instrument with Cu-Kα radiation source (1.54 Å) between 8 and 80° generated at 40 kV and 35 mA at room temperature. In addition, FT–IR spectra (4000–400 cm−1) were recorded on a Vector 22 (Bruker, Ettlingen, Germany) Fourier transform infrared spectrometer using the KBr pellet technique with a ratio sample/KBr of 1:100 by mass. The size and shape of CoFe2O4 were characterized by scanning electron microscope model LEO1430vp (LEO Electron Microscopy Inc., Carl Zeiss, Germany) and transmission electron microscope model 906 E (Zeiss, Göttingen, Germany).

The pH values were measured with a Metrohm digital pH-meter model 827 (Metrohm Ltd., Herisau, Switzerland) supplied with a glass–combined electrode. An electronic analytical balance. Mettler Toledo model PB303 (Mettler Toledo, Greifensee, Switzerland) was used to weigh the solid materials.

2.3. Synthesis of CoFe2O4 nano–particles

The CoFe2O4 MNPs was prepared according to Massart method as described elsewhere [26]. Briefly, a solution containing ferric chloride (40 mL, 1 mol L−1) and cobalt nitrate (10 mL, 2 mol L−1, in 2 mol L−1 HCl) was added to sodium hydroxide (500 mL, 0.7 mol L−1) under vigorous stirring. The obtained solution was heated at 95 °C for 30 min and then allowed to cool down to room temperature. To get free particles from sodium and chloride ions, the product was washed with dilute nitric acid, and then washed with deionized water until the pH value of supernatant was about 7–8. The as-prepared product was treated with 0.5 mol L−1 Fe(NO3)3 for 30 min, then centrifuged and washed through several cycles with deionized water. After the supernatant was discarded, the precipitation was further washed with acetone for removal of the residual water, and kept in air-dry at room temperature for 2 h. Because of the most of CL reactions proceed in the solutions; it is necessary to bring initially the solid nano–particles into a water-soluble form and then apply them to CL reactions. So, the stock solution of CoFe2O4 MNPs was obtained by adding 0.01 g of dry CoFe2O4 MNPs to 100 mL of 0.05 mol L−1 nitric acid.

To test the reproducibility of the synthesis of CoFe2O4 MNPs, three batches were prepared using the above-mentioned procedure. Then, UV–vis spectrum of 3 mg L−1 CoFe2O4 colloidal solution obtained from each batch was individually prepared and compared with each other. It was found that the UV–vis spectra are similar and the absorbance intensities at 285 nm are the same with the precision of 2.4%. Moreover, the effect of MNPs obtained from different batches on the enhancement of the H2O2–luminol CL response was also studied in the optimum conditions. The RSD (n = 3) of the obtained CL signals for luminol emission at 425 nm was 4.1%, indicating the good batch-to-batch reproducibility of the as-prepared CoFe2O4 MNPs.

2.4. Sample preparation

Water samples including tap water, bottled mineral water, underground water, spring water and photographic wastewater were chosen for the analysis. The bottled mineral water was purchased from local market and the others were collected from local sources. On arrival to laboratory, water samples were stored in refrigerator at 4 °C and proper aliquots of each sample solution were analyzed within 24 h of collection without previous treatment or filtration by following the procedure described in Section 2.5. As the concentration of Ag(I) in photographic wastewater sample was higher than the dynamic range of the developed method, appropriate dilution was made before its analysis.

2.5. General procedure

CL analyses were carried out in the batch conditions. A 1.0 mL aliquot of luminol (1.5 mmol L−1 in 0.01 mol L−1 NaOH) and 90 μL
of CoFe₂O₄ (0.1 g L⁻¹) were added into a small vial. The solution was mixed thoroughly and then an appropriate volume of standard or sample solution of Ag(I) was added and the volume was reached to 2.5 mL with deionized water. The mixture was left to react at room temperature for 5 min. Finally, to record the CL signal, the solution was transferred into a 1.0 cm spectrophluorometer cell. The CL reaction was triggered by manual injection of 0.5 mL of 6.0 mmol L⁻¹ H₂O₂ solution by a microsampler connected to a polypropylene tube. For this purpose, the tube was firstly filled with H₂O₂ solution through the microsampler and the tip of the tube was positioned at the top of the cell. Then, the cap of cell compartment was tightened and the injection was manually done by means of the microsampler. At this time, the CL intensity was recorded in a time course measurement mode.

3. Results and discussion

3.1. Characterization of CoFe₂O₄ nano-particles

Identification of the crystalline phases of CoFe₂O₄ MNPs was performed by XRD analysis and the pattern of the as-prepared material is shown in Fig. 1A. As can be seen, the diffraction peaks of prepared CoFe₂O₄ MNPs occurred at 2θ region of 30°-80° were in accordance to those of standard CoFe₂O₄ XRD pattern (JCPDS No. 22-1086), which are ascribed to crystal plate of (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (6 2 0) and (3 3 3) that are related to the spinel structure. To characterize the surface nature of the CoFe₂O₄ MNPs, the infrared absorption spectroscopy was used. The FT-IR spectrum in the region from 400 to 4000 cm⁻¹ is presented in Fig. 1B. The peak at 596 cm⁻¹ is attributed to Fe-O stretching mode and a broad band at 3320 cm⁻¹ is assigned to the stretching vibrations of Fe-O–H. Also, the band attributed to H-O–H bending mode of vibration in H₂O can be observed at 1617 cm⁻¹ in the FT-IR spectrum of CoFe₂O₄ MNPs. In addition, scanning electron microscopy was used to obtain information on the particle size and morphology of as-prepared MNPs. The size of the nano-particles should be sufficiently small to prepare stable magnetic colloids [32], SEM image of CoFe₂O₄ MNPs is shown in Fig. 1C. It can be seen that the CoFe₂O₄ nano-particles had nearly uniform distribution of particle size and the average diameter of CoFe₂O₄ MNPs was less than 50 nm. Moreover, TEM analysis of the colloidal solution reveals that both spherical and semi-spherical particle morphologies are present. The TEM images of the CoFe₂O₄ MNPs in the absence and presence of the silver ions are shown in Fig. 1D and E, respectively. In comparison with Fig. 1D, it is clear that the overall inorganic diameter increases in the presence of the silver ions, confirming the formation of CoFe₂O₄–Ag core–shell nano-particles with the average diameter of less than 100 nm.

3.2. Enhancement of luminol CL and CL mechanism discussion

Enhancement effect of CoFe₂O₄ MNPs on luminol CL was investigated by measuring the CL intensity of the mixture of luminol and H₂O₂ in the absence and presence of CoFe₂O₄ MNPs. As can be seen from Fig. 2, in the absence of CoFe₂O₄ MNPs, a weak light emission was observed. However, the CL intensity of luminol–H₂O₂ system was amplified by at least 10 times in the presence of CoFe₂O₄ MNPs. These results indicated that the weak CL intensity of luminol and H₂O₂ can be enhanced by the CoFe₂O₄ MNPs. On the other hand, the maximum emission wavelength of the system in the absence and presence of CoFe₂O₄ MNPs was around 425 nm, indicating that the role of CoFe₂O₄ MNPs is only an enhancement reagent. As a result, the enhanced CL signals were ascribed to the possible catalysis from CoFe₂O₄ MNPs.

It is well known that luminol can react with hydrogen peroxide to produce weak CL in alkaline conditions. The superoxide anion (O₂⁻•) or hydroxyl radical (OH•) is the important intermediates involved in the reaction. The OH• reacts with luminol to form luminol radical, then the produced luminol radical reacts with O₂⁻•, yielding an unstable endoperoxide and an electronically excited 3-aminophthalate anion, leading to light emission [28]. The decomposition of H₂O₂ to generate O₂⁻• and OH• could be catalyzed in the presence of CoFe₂O₄ nano-particles. It mainly results from the peroxydase-like catalytic activity of CoFe₂O₄ MNPs [26]. The resultant O₂⁻• and OH• further oxidize luminol in basic media to produce the strong CL emission. On the other hand, the CL intensity of luminol–H₂O₂–CoFe₂O₄ system could be inhibited by Ag(I) ions. Shi and co-workers [33] found that when CoFe₂O₄ MNPs are added into the mixture of luminol and AgNO₃, they could catalyze the reduction of Ag(I) ions by luminol to produce Ag atoms, which immediately cover the CoFe₂O₄ MNPs to form CoFe₂O₄–Ag core–shell nano-particles. With the continuous deposition of Ag on the surface of CoFe₂O₄ MNPs, the catalytic activity of the core–shell nano-particles could be inhibited and a decrease in CL intensity may be observed.

Considering the effect of Ag(I) concentration on CL emission described above, we can come up with a model of the catalysis process as follows: once Ag(I) ions, in the range of 0.5–100 ng mL⁻¹, were added into the mixture of luminol and CoFe₂O₄ MNPs, Ag(I) ions were reduced to Ag atoms by luminol under the catalysis of CoFe₂O₄ MNPs, which covered instantly the surface of CoFe₂O₄ MNPs and also decreased the luminal concentration in the mixture. Although the luminol radical could be reacted with the dissolved oxygen leading to the CL [33], the CL intensity was not recorded in this step. After 5 min, H₂O₂ was injected into the mixture and the CL signal of luminol–H₂O₂–CoFe₂O₄–Ag system was recorded at this time. As mentioned above, the luminal concentration is decreased due to reaction with Ag(I) and CL signal is produced by interaction of H₂O₂ with the excess of luminal in the mixture. Fig. 3a shows the CL intensity difference (ΔCL) of luminol–H₂O₂ system in the absence and presence of Ag(I) ions versus Ag(I) concentration in the range of 0.5–100 ng mL⁻¹. As can be seen, there was a slightly variation in the ΔCL value. It means that the luminal is slightly consumed when it reacts with Ag(I) due to low concentration of Ag(I) in the mentioned range. However, Fig. 3b shows the CL intensity difference (ΔCL) of luminol–H₂O₂–CoFe₂O₄ system in the absence and presence of Ag(I) ions versus Ag(I) concentration at the same concentration range. It can be seen that the CL intensity of luminol–H₂O₂–CoFe₂O₄ system is significantly decreased with the increase in Ag(I) concentration, leading to the higher ΔCL. This result further confirms that Ag(I) ion has an inhibitory effect on the peroxidase-like catalytic activity of CoFe₂O₄ MNPs, which attributed to the formation of thin layer of Ag NPs on the surface of CoFe₂O₄ MNPs [34]. It has been reported that the MNPs could be nucleation centers for core–shell NPs synthesis [35,36].

3.3. Optimization of chemiluminescence conditions

To maximize the sensitivity of the CL detection, the CL conditions were optimized. The effect of important variables such as the pH value, the concentrations of H₂O₂, luminol, CoFe₂O₄ nano-particles and incubation time on the analytical signal was studied by one-at-a-time method. A 60 ng mL⁻¹ solution of silver nitrate was used for all measurements and each experiment was repeated three times.

3.3.1. Effect of pH

In the present work, CoFe₂O₄ nano-particles were synthesized according to Massart method [26] (Section 2.3). The synthesized ferrofluid was composed of positively charged magnetic
Fig. 1. (A) XRD pattern, (B) FT-IR spectrum, (C) SEM image, (D) TEM image of CoFe$_2$O$_4$ nano-particles, and (E) TEM image of CoFe$_2$O$_4$–Ag nano-particles.
nano-particles of CoFe2O4 with nitrate counterions. However, the positive charge of the surface may be changed into negative one by adding hydroxide ions. On the other hand, the CL emission of luminol is produced in an alkaline medium. Therefore, the CL intensity of H2O2–luminol–CoFe2O4 system in the presence of Ag(I) ion mainly depends on the pH. Consequently, the effect of pH on the CL intensity was investigated in the range of 7.5–12.5 by varying the NaOH concentration of the luminol solution. As the point of zero charge for CoFe2O4 MNPs is around pH 8 [37], the surface charge of the CoFe2O4 MNPs would be negative at pH > 8. In this case, Ag(I) cations could adsorb on the surface of CoFe2O4 MNPs. Fig. 4a reveals that the CL signal increases with increasing the pH from 8.5 to 10 and remains constant between pH 10 and 11 before decreasing at pH values higher than 11. An increase in the concentration of OH− anions, leading to silver hydroxide formation at pH > 11 might be ascribed to the observed decrease in the CL signal. Accordingly, pH 10.5 was selected as the optimum pH for further experiments. For this reason, the luminol solution was prepared in 0.01 mol L−1 NaOH solution.

3.3.2. Effect of CL reagents concentrations

The effect of H2O2 concentration in the range of 0.1–5.0 mmol L−1 was investigated. According to the obtained results shown in Fig. 4b, the CL intensity increases with increasing H2O2 concentration up to 1.0 mmol L−1, and then declines evidently. This decrease may be attributed to inactivity of MNPs at higher concentrations of H2O2 [32]. The influence of luminol concentration as another CL reagent on the CL response was also examined. In the H2O2–luminol–CoFe2O4–Ag system, concentration of H2O2 must be higher than that of luminol to ensure the complete luminol consumption. On the other hand, further increase in the H2O2 concentration may be inhibited CoFe2O4 MNPs activity. Consequently, the ratio of optimum H2O2 to luminol concentration was investigated to select optimum amount of luminol. Based on the obtained results given in Fig. 4c, the highest CL response was obtained at H2O2/luminol ratio of 2. Thus, luminol concentration of 0.5 mmol L−1 was selected for further studies.

3.3.3. Effect of CoFe2O4 nano-particles concentration

The CL signal in various amounts of CoFe2O4 MNPs was studied in the range of 0.5–10 mg L−1 of colloidal solution. As it can be seen from Fig. 4d, the maximum CL response was achieved in the case of 3 mg L−1 concentration. However, higher concentrations led to a decrease in CL response, probably due to the self-absorption of the CL emission by CoFe2O4 MNPs. Hence, 3 mg L−1 of MNPs colloidal solution was selected for subsequent experiments.

3.3.4. Effect of incubation time

To investigate the effect of the reaction time, the luminol–CoFe2O4 solutions containing 60 ng mL−1 Ag(I) ion were prepared and the CL signals were recorded at different reaction times (1–10 min) before injection 0.5 mL of 6.0 mmol L−1 H2O2 solution into the reaction cell. According to the obtained results shown in Fig. 4e, the CL signal increases with the increase in incubation time up to 4 min and then reaches a constant value. As a result, the incubation time of 5 min was selected for further experiments.

3.3.5. Effect of temperature and stability of the method

The effect of temperature on the CL signal was investigated. It was found that the CL response remains constant in the temperature range between 20 °C and 50 °C. Accordingly, the room temperature was chosen as an operational temperature for the further experiments. Regarding the stability of CoFe2O4 MNPs, acidic soils are not chemically stable in time. Therefore, the nano-particles are progressively destroyed in acidic medium and the soil flocsultes [37]. However, as we mentioned previously, the CoFe2O4 MNPs show an amphoteric behavior so that the positive charge of the surface could be changed into negative one by adding hydroxide ions. In this case, a stable alkaline sol may be prepared. So, in the present study, the synthesized CoFe2O4 MNPs were chemically stable in time due to the nature of the luminol reaction, which is more favored under basic conditions.

3.4. Study of interferences

To explore the utility of CoFe2O4 MNPs-intensified H2O2–luminol CL system as a ion-selective CL chemosensor for Ag(I), the competition experiments were also conducted in the presence of Fe3+, Co2+, Ni2+, Cu2+, Cr3+, Zn2+, Pb2+, Cd2+, Hg22+, and Al3+ ions. For this purpose, the same concentration (60 ng mL−1) of the mentioned metal ions was individually added into the luminol–CoFe2O4 MNPs solution and under the optimized conditions the CL reaction was triggered by injection of H2O2 into the reaction cell. As shown in Fig. 5, unless about Ag(I) ion, no significant variation in CL intensity of H2O2–luminol–CoFe2O4 MNPs system was found in the presence of other ions. Moreover, the tolerance limits of some potentially interfering ions on the determination of Ag(I) ion were investigated. In these experiments, different amounts of ions were added to the test solutions containing 60 ng mL−1 of Ag(I) and then followed according to the general procedure. The tolerance limits of the interfering ions, defined as the maximum concentration of the interfering ion causing a change in the analytical signal less than ±5%, when compared with the signal of 60 ng mL−1 Ag(I) alone, are given in Table 1. These

![Fig. 2. CL spectrum of luminol–H2O2 system (a) in the absence and (b) presence of CoFe2O4 nano-particles.](image)

![Fig. 3. (a) CL intensity difference (ΔI/ΔI0) of luminol–H2O2 system in the absence and presence of Ag(I) ions versus Ag(I) concentration in the range of 0.5–100 ng mL−1, and (b) CL intensity difference (ΔI/ΔI0) of luminol–H2O2–CoFe2O4 system in the absence and presence of Ag(I) ions in the range of 0.5–100 ng mL−1.](image)
Fig. 4. Effect of (a) pH, (b) H₂O₂ concentration, (c) luminol concentration, (d) CoFe₂O₄ MNPs concentration, and (e) reaction time on CL intensity of H₂O₂–luminol–CoFe₂O₄ system in the presence of 60 ng mL⁻¹ Ag(I) ion.

Table 1
Tolerance limits of interfering ions in the determination of 60 ng mL⁻¹ of Ag(I).

<table>
<thead>
<tr>
<th>Potentially interfering ions</th>
<th>Interferent to analyte ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄³⁻, Bi³⁺, Zn²⁺, CH₃COO⁻, Ce⁴⁺</td>
<td>800:1</td>
</tr>
<tr>
<td>Mg²⁺, Ca²⁺, Al³⁺, NO₃⁻, NH₄⁺</td>
<td>500:1</td>
</tr>
<tr>
<td>Ni²⁺, Cr³⁺, Cl⁻, F⁻, SO₄²⁻, K⁺, Na⁺</td>
<td>300:1</td>
</tr>
<tr>
<td>Cu²⁺, Co²⁺, MnO₄⁻</td>
<td>100:1</td>
</tr>
<tr>
<td>Pb²⁺, Fe⁴⁺, Fe²⁺, Hg⁺, Cd²⁺</td>
<td>50:1</td>
</tr>
</tbody>
</table>

results indicate that the selectivity of the presented chemosensor is very high in the case of Ag(I) ion.

3.5. Analytical figures of merit

The calibration graph was constructed by applying the general procedure for different concentration of silver ion under the optimum conditions. A linear calibration graph was obtained in the range of between 0.5 and 100 ng mL⁻¹, with a correlation coefficient of 0.9990. The regression equation of the calibration graph was ΔI₁CL = 1.3386 C₁Ag(Ⅰ) + 0.8685, where ΔI₁CL is the corrected
3.6. Real sample analysis

The application of the presented method was evaluated by the determination of trace levels of Ag(I) in several water samples, i.e., bottled mineral water, tap water, underground water, spring water and photographic wastewater. Recovery experiments were performed to evaluate the accuracy of the method. The obtained results are summarized in Table 3. Statistical analysis of the obtained results using Student t-test showed that there is no significant difference between added and found values. The photographic wastewater was also analyzed by flame atomic absorption spectroscopy (FAAS) as an independent method. The deviation of the blank and m is the slope of the calibration curve) were 0.15 ng mL⁻¹ and 0.5 ng mL⁻¹, respectively. The precision of the method was evaluated by repeated analysis of Ag(I) ion during the course of experimentation on the same day and on different days under the optimized experimental conditions. For both intra-day and inter-day variation, solutions of Ag(I) ion at concentrations of 60 ng mL⁻¹ were determined in triplicate. The % RSD (n = 6) for intra-day and inter-day analysis were found to be 3.2% and 4.1%, respectively. Comparative information from some studies on determination of Ag(I) by different analytical methods for the figure of merits is given in Table 2. In comparison with other reported methods, the luminol–H₂O₂–CoFe₂O₄ system has relatively good RDS and excellent LOD for silver(I) determination.

Table 3: Determination of Ag(I) in water samples (result of recoveries of spiked samples with different amounts of Ag(I)).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added Ag(I) (ng mL⁻¹)</th>
<th>Found Ag(I)³ (ng mL⁻¹)</th>
<th>Recovery (%)</th>
<th>t-Statistic⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>40.0</td>
<td>41.3 ± 1.7</td>
<td>103.2</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>77.5 ± 3.6</td>
<td>96.9</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Spring water</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>40.0</td>
<td>41.0 ± 2.3</td>
<td>102.5</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>81.0 ± 2.0</td>
<td>101.2</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Underground water</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>40.0</td>
<td>39.6 ± 2.3</td>
<td>99.2</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>79.0 ± 2.1</td>
<td>98.7</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>Bottled mineral water</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>40.0</td>
<td>38.6 ± 2.4</td>
<td>96.5</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>80.0</td>
<td>76.0 ± 4.0</td>
<td>95.0</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>Photographic wastewater</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4.0</td>
<td>21.5 ± 1.4</td>
<td>102.5</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>25.5 ± 1.2</td>
<td>101.2</td>
<td>0.14</td>
<td></td>
</tr>
</tbody>
</table>

³ Mean of three experiments ± standard deviation.
⁴ t-Critical = 4.3 for n = 2 and P = 0.05.
⁵ From drinking water system of Azarshahr, Iran.
⁶ Obtained from local source, Azarshahr, Iran.
⁷ Obtained from local market, Azarshahr, Iran.
⁸ Added and found concentrations are in µg mL⁻¹.

*Fig. 5. Effect of some metal ions on the CL intensity of luminol–H₂O₂–CoFe₂O₄ system. The concentrations of all metal ions are 60 ng mL⁻¹. Other conditions: [luminol]=0.5 mmol L⁻¹, [H₂O₂]=1.0 mmol L⁻¹, [CoFe₂O₄]=3 mg L⁻¹ and pH 10.5.*
silver concentration in the photographic wastewater was obtained 17.82 ± 0.25 μg mL⁻¹. The obtained results from both of them demonstrate statistical equivalence using the paired t-test (2-tail) confirming there is no significant difference between the results at a 95% confidence limit. This result suggests that the presented method has a great potential for the sensing of Ag(I) in environmental samples.

3.7. Advantages of the method

Although heavy and transition metal ions are relatively easy to chelate and detect in organic solvents, they are rather difficult to recognize directly in aqueous environments due to their strong hydrazides. In this work, a simple and environment-friendly chemosensor has been introduced for recognition of silver ions in aqueous solutions, which is based on the inhibitory effect of Ag(I) ion on the enhanced chemiluminescence signal of H₂O₂–luminol system in the presence of the cobalt ferrite magnetic nanoparticles. The developed method was successfully applied for the recognition and monitoring of low concentrations of silver ions in several water samples without previous treatment or pre-concentration with time-consuming and laborious extraction techniques. Under the optimum conditions, the chemosensor can detect as low as 0.15 ng mL⁻¹ Ag(I) ion, which is lower than the previously reported works. In conclusion, the developed method is a simple, fast, stable, non-expensive, sensitive and selective method for the sensing of silver ions in aqueous solutions.

4. Conclusions

In this research, a simple, selective and sensitive chemosensor was introduced for the detection of Ag(I) ion. The potential of magnetic nano-particles as catalysts for chemiluminescence in aqueous solutions was demonstrated using a luminol–H₂O₂ CL reaction as a model. It was found that the CL radiation emitted during the oxidation of luminol by hydrogen peroxide catalyzed by the CoFe₂O₄ MNPs is at least 10 times larger than that of without CoFe₂O₄ MNPs. On the other hand, our experiments show that the CL intensity of luminol–H₂O₂–CoFe₂O₄ system decreases in the presence of Ag(I) ion due to its inhibitory effect on catalytic activity of the CoFe₂O₄ MNPs via the reduction of Ag(I) ions to Ag atoms by luminol and covering the surface of the MNPs with the produced Ag atoms. As the extent of inhibition is proportional with Ag(I) ion concentration, a new chemosensor was developed for the determination of trace levels of Ag(I) ion in aqueous solutions. The presented method promises high sensitivity and good reproducibility for Ag(I) ion detection and was successfully used to determine Ag(I) ion in several water samples.

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References

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