Novel catalytic determination of cobalt(II) using oxidation of silver nanoparticles by hydrogen peroxide

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ABSTRACT

The ability of surface plasmon resonance (SPR) to the catalytic determination of Co(II) was exploited here using oxidation of silver nanoparticles (AgNPs) as a chromogenic reagent with hydrogen peroxide (H_2O_2). The reaction was followed, spectrophotometrically, by tracing the AgNPs at 405 nm within 5 min after the initiation of reaction. Under the optimal experimental conditions, detection limit and relative standard deviation were 3 ng mL^{-1} and 4.6% (1.0 µg mL^{-1}; n=7), respectively. The plot of initial reaction rates as a function of Co(II) concentration was linear in the ranges of 6 to 60 ng mL^{-1} and 0.6 to 350 µg mL^{-1}.
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KEYWORDS

Cobalt;
Surface plasmon resonance;
Silver nanoparticles;
Hydrogen peroxide.

INTRODUCTION

Cobalt is very important mineral element for environmental chemistry and human biochemical metabolism[1,2]. Low concentrations of cobalt in living organism and in the environment make it very difficult for analytical determination and therefore often preconcentration steps are necessary[3,4]. Different spectroscopies and electrochemical techniques have been used for cobalt determination[5-9]. Catalytic methods with spectrophotometric monitoring for Co(II) determination are also reported[10-14]. Catalytic kinetic methods

have the advantages of low cost apparatus, rapid analysis and extremely low detection limits comparable with those of the instrumental methods[11-13]. Most of these methods are based on the catalytic action of cobalt on the oxidation of various organic reagents. This work reports the first application of AgNPs as chromogenic reagent to the determination of Co(II) ions using spectrophotometric technique. The procedure uses is based on the reaction of H_2O_2 with the AgNPs and catalytic effect of Co(II) on redox reaction of them. This method is rapid, simple, selective, and sensitive and uses only AgNPs as reagent.

EXPERIMENT

Apparatuds

A GBC UV-Visible Cintra 6 Spectrophotometer model, attached to a Pentium (IV) computer, with 1-cm quartz cells was used for the evaluation of optical characteristics of the surface plasmon resonance (SPR) of AgNPs and recording kinetic spectrophotometric data. Metrohm 781 pH-meter was used to adjust pH of the buffered solutions.

Reagent and solution

All chemicals were of analytical grade and used as received without further purification. Cobalt nitrate hexahydrous $(Co(NO_3)_2 \cdot 6H_2O)$ and H_2O_2 solution (30%) were purchased from Merck. Silver nitrate $(AgNO_3)$, sodium borohydride $(NaBH_4)$ and soluble starch used for the synthesis of AgNPs. The starch-stabilized AgNPs were prepared according to previous reported method with minor modification[15].

Procedure

All the measurements were performed at 25.0 ± 0.1 °C. The redox reaction was monitored spectrophotometrically by measuring the change of absorbance of the reaction mixture at 405 nm that is λ_{max} of SPR peak of AgNPs at these conditions against a reagent blank, as shown in Figure 1. The fixed time method (4.0 min from the initiating of reaction) was used to obtain the signal.
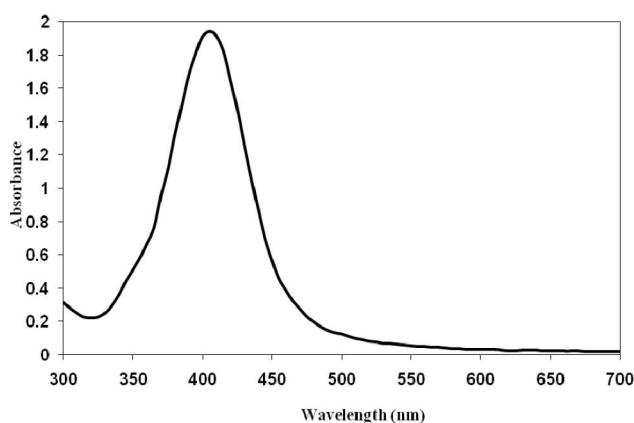

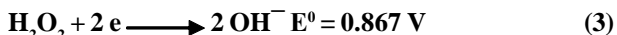**Figure 1 : The SPR spectrum of starch-stabilized AgNPs.**

In a typical procedure, two steps were involved. First, 2.0 mL of KH_2PO_4 buffer solution (pH 7.0), 1.0 mL of AgNPs solution $(1.0 \times 10^{-3}$ mol $L^{-1})$ and appropriate volumes of Co(II), in the range of $0.005 - 500.0 \, \mu g \, mL^{-1}$

were transferred to 10-mL volumetric flasks and made up to the mark with deionized water. Second, for each measurement, 1.0 mL of the above solution was transferred to a 1-cm quartz cell, then, 10 μL of H_2O_2 solution $(5 \times 10^{-2}$ mol $L^{-1})$ was injected to the cell by microsyringe and after vigorous stirring, immediately, the initial absorbance (A_i, λ_{max}) was recorded at 405 nm and after 4 min, final absorbance (A_f) was measured. The net values $(\Delta A = A_i - A_f)$ were obtained by using standard Co(II) solutions. Calibration graphs were made based on the fixed time method by plotting the net values of absorbance versus cobalt(II) concentration.

RESULTS AND DISCUSSION

Preliminary investigations of the system

AgNPs initially react with H_2O_2 to form Ag^+ and our experimental results show that AgNPs reactivity towards H_2O_2 varies significantly with pH. H_2O_2 is powerful oxidizing agent and its standard redox potential is dependent on the pH value of the solution:

$$H_2O_2 + 2\,AgNPs \longrightarrow 2\,Ag^+ + 2\,O\,H^- \qquad (1)$$

$$H_2O_2 + 2\,H^+ + 2\,e \longrightarrow 2\,H_2O \quad E^0 = 1.763\,V \qquad (2)$$

$$H_2O_2 + 2\,e \longrightarrow 2\,OH^- \quad E^0 = 0.867\,V \qquad (3)$$

Under both conditions, acidic and neutral, the electrochemical potentials are higher than that of Ag^+/Ag ($E^0 = 0.7996$ V). Therefore, H_2O_2 can act as an effective oxidant for AgNPs.
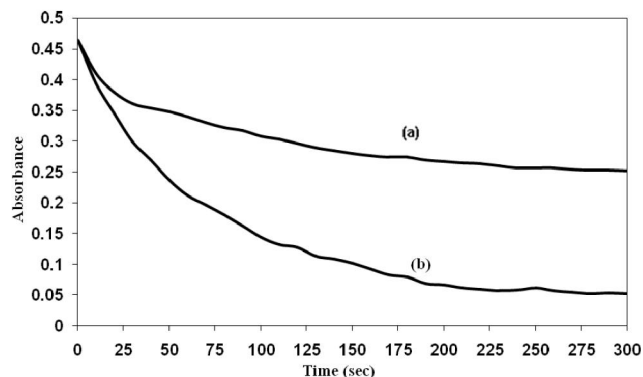
The silver NPs were stable in yellow color. The absorption peak at 405 nm reduced by increasing Co(II) concentration in the presence of H_2O_2 with a color change of light yellow to colorless. Figure 2 shows the changes of absorbance at 405 nm during different time periods for both the catalytic and non-catalytic oxidation reactions of AgNPs by H_2O_2. It could be concluded that Co(II) has a catalytic effect on the oxidation of AgNPs by H_2O_2 to form Ag^+. As can be seen in Figure 2, there was a significant variation in the absorbance value for the uppermost reaction up to 240 seconds.
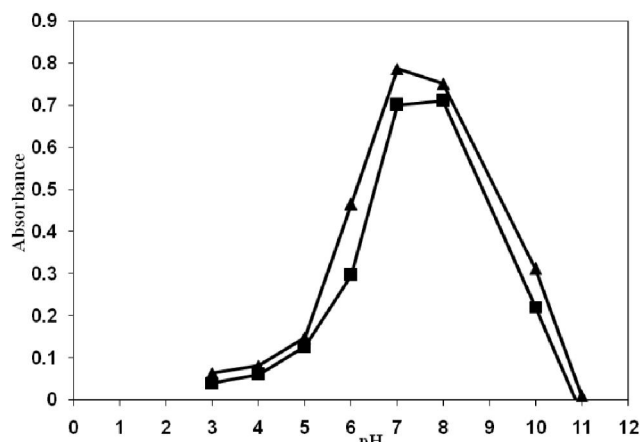
Effect of pH

The effect of pH over the ranges of 3.0 to 11.0 on the SPR band intensity of oxidation of AgNPs by H_2O_2 at presence and absence of Co(II) is investigated (Figure 3). Maximum intensity of SPR peak at 405 nm was

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observed at pH 7.0 for both non-catalyzed and catalyzed reactions. The decrease in the SPR band intensity at pH>7 is probably due to the Ag_2O formation. Thus, pH of 7.0 was selected as the optimum pH for further studies.

Figure 2: Typical absorbance-time plot at 405 nm for the reaction of AgNPs with H_2O_2 in the absence (a) and at presence (b) of Co(II). Conditions: 1.0×10^{-4} mol L^{-1} AgNPs; 5.0×10^{-5} mol L^{-1} H_2O_2; 6 ng mL^{-1} Co(II); pH 7.0; 25 °C.

Figure 3: Effect of pH on the absorbance of AgNPs with H_2O_2 in the absence (a) and at presence (b) of Co (II). Conditions as in Figure 2.

Analytical parameters

A plot of initial reaction rates as a function of Co(II) concentration (Figure 4), was linear in the ranges of 6 to 60 ng mL^{-1} and 0.6 to 350 µg mL^{-1} according to the equations:
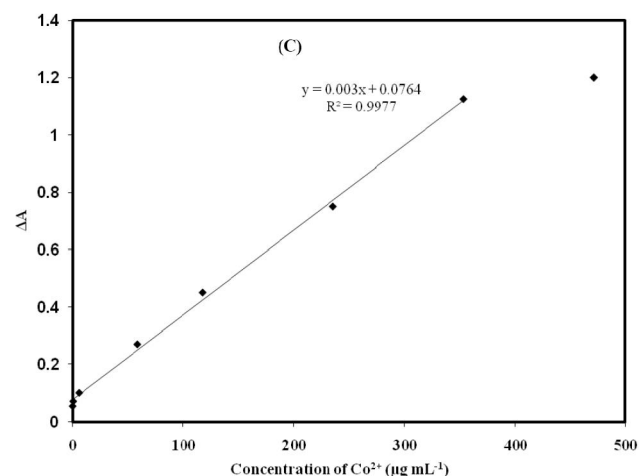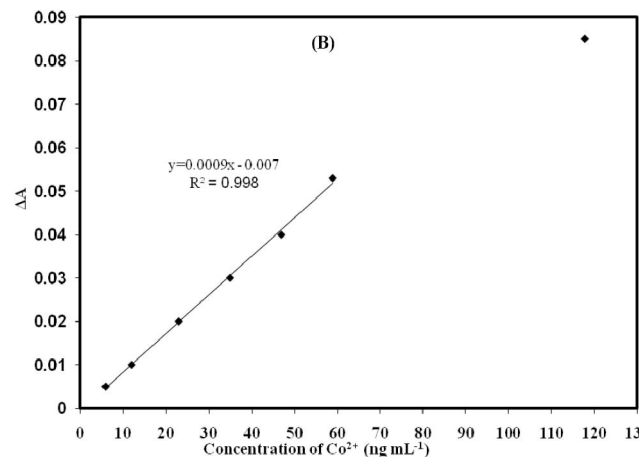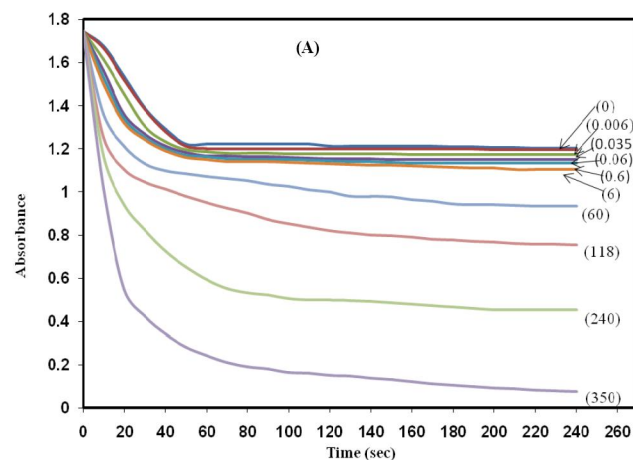
$A = 0.0009\ C_n - 0.007$ (R = 0.9981 for n = 6)

and

$A = 0.003\ C_m + 0.076$ (R = 0.9977 for n = 5)

where, A, R, C_n and C_m are absorbance, correlation coefficient, concentration of Co(II) in ng mL^{-1} and concentration of Co(II) in µg mL^{-1}, respectively. The de-

tection limit, defined as the average of the blank value plus three times of its standard deviation and relative standard deviation were 3 ng mL^{-1} and 4.6% (1.0 µg mL^{-1}; n=7), respectively.

Figure 4 : Net value absorbance -time curves for the reaction of AgNPs with H_2O_2 at different concentrations (µg mL^{-1}) of Co(II) (A) and fixed time calibration curves for determination of Co(II) (B,C).

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Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the reaction rate of a fixed AgNPs concentration (1.0×10^{-4} mol L^{-1}) for both non-catalyzed and catalyzed reactions investigated according to the above procedure. There was a significant variation in the net values ($\Delta A = A_i - A_f$) for the uppermost reaction up to 5×10^{-5} mol L^{-1} H_2O_2. Therefore, a concentration of 5×10^{-5} mol L^{-1} H_2O_2 was selected as the optimum concentration for further studies.

Effect of co-existing ions

The possibility of water constituents, such as Na^+, K^+, Ca^{2+}, Ba^{2+}, CH_3COO^-, NO_3^-, HPO_4^{2-}, Ni^{2+}, etc. interfering with Co(II) for its catalytic effect was considered. The following excess of ions did not interfere in the measurement (i.e., caused a relative error of less than 5%): more than 1000-fold of Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, CH_3COO^- and NO_3^-; 100-fold of NH_4^+, HCO_3^-, SO_4^{2-}, Fe^{3+} and Al^{3+}; 50-fold of Mn^{2+}, Ni^{2+}, Zn^{2+}, Zn^{2+}, Fe^{2+}, Cr^{3+} and Bi^{3+}; 20-fold of Pb^{2+}, Cu^{2+} and Cd^{2+}; 10-fold of $C_2O_4^{-2}$; 1-fold of Hg^{2+}. The results showed that most of the investigated ions do not interfere in the catalytic oxidation reaction; only Hg^{2+} appeared to interfere with of trace amounts of Co(II) in real samples.

Application to real samples

In order to validate the analytical capability or to establish the reliability and applicability, the present method was applied for the determination of Co(II) in different water samples. The results of TABLE 1 indicate that the Co(II) recoveries from the samples were quantitative, which shows that cobalt could be determined in the specified concentration range in real samples.

TABLE 1 : Recoveries results for Co(II) determination in different water samples

Sample	Present method (μg mL^{-1})[a]	Spiked Co^{2+} (μg mL^{-1})	Found Co^{2+} (μg mL^{-1})[a]	Recovery (%)
Tap water	BLR[a]	2.0	2.06±0.7	103.0
Drinking water	BLR	2.0	2.09±0.5	104.5
Waste water[c]	17.6±0.6	2.0	20.73±0.9	105.7

[a]**Mean of three determinations ± standard deviation;** [b]**Bellow of linear range;** [c]**After dilution by 200 times**

CONCLUSION

In this paper, a new catalytic reaction for determination of Co(II) based on the ability of SPR, i.e., oxidation of AgNPs with H_2O_2, is proposed. The kinetics of this reaction was followed by spectrophotometry the AgNPs and the results indicate that the proposed method is satisfactory for the determination of the cobalt in different water samples. The reaction gives a low limit of detection of 3 ng mL^{-1}.

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