

Sulu Çözeltilerde Hg²⁺ Tespiti için Sinamaldehit Türevi Bir Kolorimetrik Sensör

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ÖZET: Ağır metal iyonları insan gıda zincirine girdiklerinde insanın merkezi sinir sistemine, karaciğerine, böbreğine, kemiğine ve dişlerine ciddi zararlar vermektedir. Bu nedenle, toksik metal iyonlarının basit, hızlı, hassas ve düşük maliyetli tanımlanması için yeni tekniklerin geliştirilmesi halk sağlığının iyileştirilmesi için gereklidir. Ağır metal iyonlarının kolorimetrik sensörler yardımıyla çıplak gözle algılanması, her insan tarafından uygulanabilirliği nedeniyle önem taşımaktadır. Bu çalışmada, kolay uygulama potansiyeli olan 3-methyl-4-((3-phenylallylidene)amino)phenol (SAR) bileşiğinin sensör özelliği incelenmiştir. Sensörün yapısı, ¹H NMR, ¹³C NMR ve kütle spektrometresi ile doğrulanmıştır. Uygulamalarda, ilk olarak sensörün rengi metal iyonlarıyla / metal iyonları olmadan karşılaştırılmış, daha sonra ölçümler UV-Vis spektrofotometresinde yapılmıştır. UV-Vis spektroskopik çalışmaları, SAR'ın MeOH (metanol) / H₂O (su) (v/ v 1: 1) içerisinde Hg²⁺ iyonlarına yüksek seçicilik ve duyarlılığı gösterdiğini ortaya koymuştur. Sensör, sarıdan pembeye renk değiştirerek Hg²⁺ iyonlarını algılamıştır. SAR ve Hg²⁺ arasındaki kompleks stokiyometrisi, Job yöntemi ve 528 nm'de UV-Vis titrasyon değerleri kullanılarak hesaplanmış ve 2:1 olarak bulunmuştur. Bağlanma sabiti $1.56 \times 10^{12} \text{ M}^{-2}$ olarak bulunmuştur. Ayrıca, sensör ve Hg²⁺ arasındaki bağlanma tersinirdir. Tespit sınırı da belirlenmiş ve $7.89 \times 10^{-6} \text{ M}$ olarak hesaplanmıştır.

Anahtar Kelimeler: Sinamaldehit, kolorimetrik, Hg²⁺, sensör

A Cinnamaldehyde-based Colorimetric Sensor for Hg²⁺ Detection in Aqueous Solutions

ABSTRACT: When heavy metal ions join the human food chain, they cause severe harm to the human liver, bone, kidney, teeth, and central nervous system. Therefore, the development of new techniques for rapid, easy, simple, reliable, and low-cost identification of toxic metal ions is a key point for improving public health. Naked eye detection of hazardous metal ions with colorimetric sensors has been gained attention due to its applicability among common people. In this study, the sensor properties of 3-methyl-4-((3-phenylallylidene)amino)phenol (SAR) were investigated. The structure of the sensor were verified by Mass spectrometry, ¹H NMR, and ¹³C NMR. In the applications, firstly the color of the sensor was compared with/without metal ions, then the measurements were made in the UV-Vis spectrophotometer. UV-Vis spectroscopic studies exhibit that SAR shows excellent sensitivity and selectivity to Hg²⁺ ions in MeOH (methanol) / H₂O (water) (v/v, 1:1). SAR can detect Hg²⁺ ions by color change from yellow to pink. Job's method and UV-Vis titration values at 528 nm were used to determine the complex stoichiometry between SAR and Hg²⁺ and the complex (SAR/Hg²⁺) stoichiometry was found to be 2:1. The binding constant was found to be $1.56 \times 10^{12} \text{ M}^{-2}$. Additionally, the binding between the sensor and Hg²⁺ was reversible. The limit of detection was also determined and calculated as $7.89 \times 10^{-6} \text{ M}$.

Keywords: Cinnamaldehyde, colorimetric, Hg²⁺, sensor

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INTRODUCTION

With the development of industrial technology, significant pollution of water, air and soil emerges as a major problem for public health. In addition, enormous quantity of heavy metals pollution has been produced to living environment owing to their widely use in industrial sectors (Tchounwou et al., 2012; Masindi and Muedi, 2018). Mercury(II) (Hg²⁺) is one of most lethal heavy metal ions, and it is commonly found in soil, water, and air of daily living environments (Bhand and Sarkar, 2005). Hg²⁺ ions are very toxic even at low concentrations and it easily bond with thiol groups found in amino acids and some enzymes (De Silva et al., 2002; Rubino, 2015). It causes great irreversible damage in humans by affecting the central nervous system and cardiovascular organs (Houston, 2011; Azevedo et al., 2012). Therefore, there has been great interest in the development of fast, efficient, and high throughput methods to monitor Hg²⁺ ions level in environment. Compared to time-consuming and expensive methods such as inductively coupled plasma mass spectrometry (ICP-MS) (Passariello et al., 1996), atomic absorption spectroscopy (Erleben and Ruzicka, 2005), and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Han et al., 2006), optical methods (fluorometric or colorimetric) are all widely preferred due to their advantages including inexpensive, simplicity in use and simple sample pretreatment.

In recent years, several fluorescent sensors have been reported for the detection of Hg²⁺ such as coumarin-based (Chen et al., 2019; Cao et al., 2019), rhodamine-based (Aydin et al., 2014; Hong et al., 2019), perylene-based (Chen et al., 2020), and pyroazole-based (Tigreros and Portilla, 2020) sensors. Most recently, colorimetric sensors have been gaining interest owing to their applicability by common people (Upadhyay et al., 2019). However, most of these sensors have some weak points such as high detection limit, low selectivity and poor sensitivity, and synthetic difficulty. In order to develop better colorimetric sensors, Schiff base derivatives have gained much importance for specific metal ions because of their simple synthetic routes, rapid response time, high selectivity and low detection limit (Berhanu et al., 2019). Recently, some interesting Schiff base derivatives have been synthesized. Specifically, cinnamaldehyde-based Schiff base derivatives have been reported for the monitoring of metal ions such as Cu²⁺ (Aydin and Keles, 2020a), Cd²⁺ (Aydin and Keles, 2020b), Ag⁺ (Kang et al., 2018), Ni²⁺ (Peralta-Dominguez et al., 2015), Al³⁺ (Kar et al., 2015; Aydin and Keles, 2017) Cu²⁺/Hg²⁺ (Cho et al., 2019).

Herein, a cinnamaldehyde-based sensor SAR was synthesized and its sensor features were studied. In the applications, firstly the color of the sensor was compared with/without metal ions, then the measurements were collected in the UV-Vis spectrophotometer. UV-Vis spectroscopic studies reveal that SAR exhibited high sensitivity and selectivity to Hg²⁺ ions in MeOH/H₂O (v/v, 1:1). SAR can detect Hg²⁺ ions by color change from yellow to pink. Job's method and UV-Vis titration values at 528 nm were used to determine the complex stoichiometry between SAR and Hg²⁺ and it was found to be 2:1. The binding constant was determined to be $1.56 \times 10^{12} \text{ M}^{-2}$. The limit of detection was also determined and calculated as $7.89 \times 10^{-6} \text{ M}$.

MATERIAL AND METHOD

Chemicals and Instrumentation

Cinnamaldehyde and 4-amino-m-cresol were obtained from Sigma-Aldrich. The other chemicals used and the solvents in the experiments were commercially obtained. The solution of Fe³⁺ and Fe²⁺ was prepared separately by dissolving in 0.1 M HCl. The solutions of the metal ions used were prepared in deionized water from chloride salts or nitrate salts of them. Stock solution of SAR (1 mM) was prepared separately in MeOH and diluted to 100 μM with MeOH/water (v/v, 1:1). A NMR spectrometer (a Bruker

NMR spectrometer (Bruker Ultra shield Plus Biospin Avance III 400 MHz NaNoBay FT-NMR)) was used to record ¹H and ¹³C NMR spectra. Shimadzu UV-1800 spectrophotometer was used to record UV-Vis spectra. An Agilent LC-MS/MS Triple Quadrupole mass spectrometer was used to perform ESI-MS analyses. The pH measurements were collected using a Corning pH meter.

Synthesis of 3-methyl-4-((3-phenylallylidene)amino)phenol (SAR)

Cinnamaldehyde (0.37 mL, 2.85 mmol) and 4-amino-m-cresol (345 mg, 2.85 mmol) were dissolved separately in 5 mL ethanol and mixed for 2 hours at room conditions while stirring. The yellow solid was filtered with a filter paper and it was then washed with cold ethanol (2x10 mL). Yield 0.55 g (82%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, 1H, N=CH), 7.74 (dd, 2H), 7.50 – 7.16 (m, 5H), 7.22 (d, 1H), 7.18 (d, 1H), 6.81 (d, 1H), 2.11 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.72, 154.68 (N=C), 146.47, 143.98, 143.27, 135.64, 134.00, 129.59, 128.52, 127.56, 119.07, 117.58, 18.07. ESI-MS (positive mode) found m/z 238.2 [SAR+H]⁺, calculated for C₁₆H₁₅NO [SAR] 237.1.

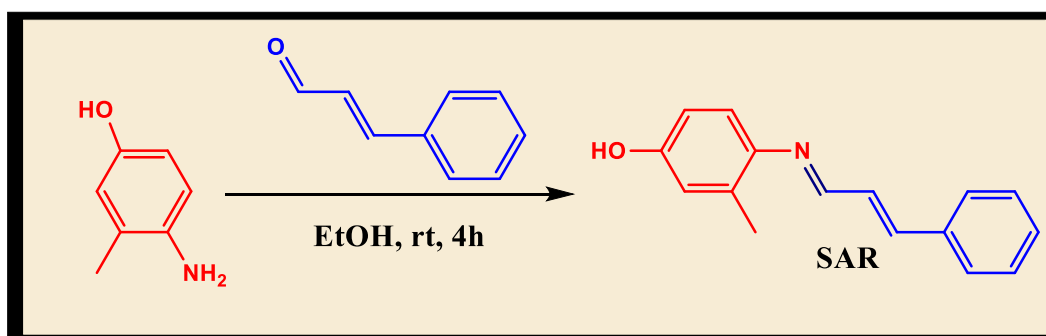
Procedures for UV-Vis studies

SAR (4.75 mg, 0.02 mmol) was dissolved in MeOH (20 mL) and 200 μL of the sensor was diluted to 1.800 mL MeOH/H₂O (v/v, 1:1) to make final concentrations of 100 μM. For each spectrum, 1.5 mL volume of the sensor solution was added to a quartz cuvette, and different stock solutions of cations were gradually added into the cuvette by using a micro-pipette. All absorption spectra were collected ranging between 300-850 nm. Upon addition of each metal ion tested to the sensors solutions, the spectral readings were recorded at ca. 5 minutes.

RESULTS AND DISCUSSION

Sensor Design and Synthesis

The sensor SAR, combining a cinnamaldehyde moiety (chromophore) and a Hg²⁺ receptor moiety formed by a nitrogen motif was designed for a colorimetric sensor for Hg²⁺. It is expected that there would be appearance intramolecular charge-transfer (ICT) (Xue et al., 2019; Aydin and Keles, 2020) between SAR and Hg²⁺ with following a significant color change and spectral change. The sensor, SAR, was synthesized in a one-step procedure (Scheme 1) and the sensor was characterized by mass spectrometry, ¹³C NMR, and ¹H NMR.



Scheme 1. Synthesis of SAR

Spectroscopic and Selectivity Studies

For the metal selectivity experiments of the sensor, 100 μM of the sensor and 100 μM of Hg²⁺, Fe³⁺, Fe²⁺, Cu²⁺, Cu⁺, Zn²⁺, Pb²⁺, Ag⁺, Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺, Al³⁺, and Cd²⁺; 250 μM for Na⁺, Ca²⁺, Mg²⁺ and K⁺ in a cuvette in MeOH / H₂O (v: v, 1: 1) system were mixed separately, and the colors of the sensor before and after metal adding were compared. As shown in Figure 1a, the color of the sensor, which was initially yellow, turned into pink color following the addition of Hg²⁺.

Next, the absorption spectra of SAR with metal ions including Hg²⁺, Fe³⁺, Fe²⁺, Cu²⁺, Cu⁺, Zn²⁺, Pb²⁺, Ag⁺, Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺, Al³⁺, Cd²⁺, Na⁺, Ca²⁺, Mg²⁺, and K⁺ were collected. The solution of SAR alone (100 μM) shows an absorption maximum at 354 nm ($\epsilon = 2.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, only SAR). The addition of Hg²⁺ to this solution caused a decrease by providing absorption of maximum at 528 nm ($\epsilon = 2.05 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$, SAR and Hg²⁺ 1:1 ratio) (Figure 1b), showing that the sensor gives a response to only Hg²⁺. The color change and the shift in wavelength are both clear indications of the intramolecular charge transfer (ICT) process during the complexation (Cesaretti et al., 2019; Aydin and Keles, 2020).

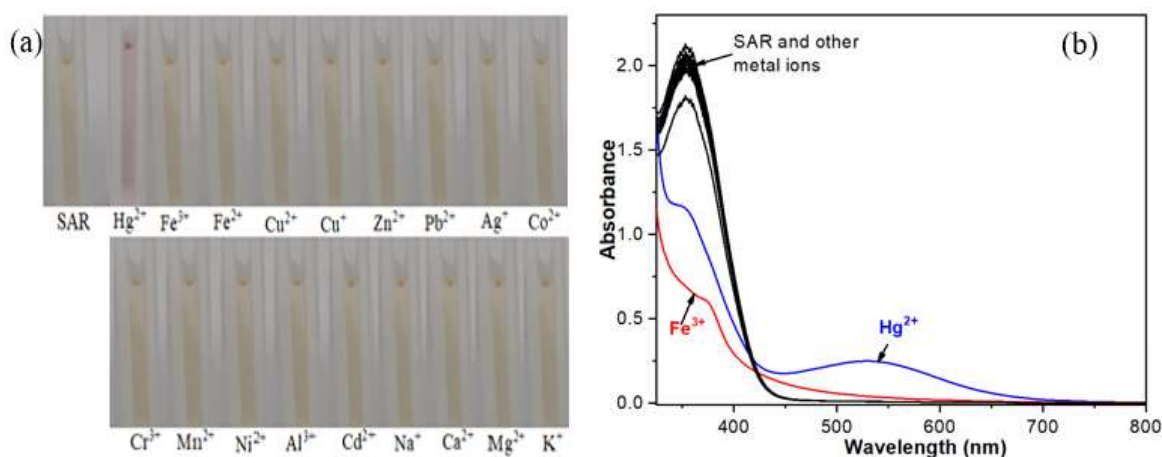


Figure 1. (a) Change in color of 100 μM NBAR with the metal ions tested (100 μM). (b) Absorption intensities of 100 μM SAR to different metal ions (100 μM for Hg²⁺, Fe²⁺, Fe³⁺, Cu²⁺, Cu⁺, Pb²⁺, Zn²⁺, Ag⁺, Co²⁺, Cr³⁺, Mn²⁺, Ni²⁺, Al³⁺, and Cd²⁺; 250 μM for Mg²⁺, Ca²⁺, Na⁺, and K⁺) in MeOH/H₂O (v/v, 1:1)

Since there is a nitrogen atom in the binding parts of the sensor, SAR, it may give a response to hydrogen ions. The effect of pH on SAR and SAR + Hg²⁺ was studied in the range of 1-10 pH. HCl (0.1 M) and NaOH (0.1 M) solutions were used to adjust pH of the sensor and the complex. As seen in Figure 2a, SAR did not give response to hydrogen ions in the pH range of 5-9. However, at pH 1-3 the sensor is not stable and it responds to H⁺ ions at pH 4. The pH of the sensor MeOH / H₂O (1:1 v/v) mixture is 6.63 and the pH of SAR + Hg²⁺ pH is 6.20. These results show that pH does not affect the selectivity between the sensor and Hg²⁺.

Competition experiments were also carried out to confirm the high selectivity of the detection system. First, the metal ions tested (200 μM) were pre-incubated with SAR (100 μM). No notable change has been observed as expected (gray bars in Figure 2b). However, the addition of Hg²⁺ (100 μM) to each of them caused an increase in the absorption intensity at 528 nm (blue bars in Figure 2b). These results reveal that competitive metal ions used (higher concentration than SAR) did not affect the selectivity of SAR to Hg²⁺.

Binding Studies between Hg²⁺ and SAR

UV-Vis titration results and Job's method were used to understand the stoichiometry between Hg²⁺ and SAR. Hg²⁺ ions at different concentrations were added to the solution of SAR (100 μM), and UV-Vis spectra were collected after each addition. While the peak of SAR at 365 nm decreased with the increasing concentration of Hg²⁺, the peak caused by the SAR-Hg²⁺ complex increased at 528 nm. As shown in Figure 3a, the absorbance titration plot showed a typical sigmoidal curve. It was saturated

when 0.5 equivalent of Hg^{2+} was used. This titration experiment shows that the binding between SAR and Hg^{2+} is 2:1. Job's method was used such that total concentrations of Hg^{2+} and NSAR were $100 \mu\text{M}$ and their absorbance intensities were collected at 528 nm . As can be seen in Figure 3b, $[(\text{Hg}^{2+}) / (\text{Hg}^{2+} + \text{SAR})]$ ratio was found to be 0.33, and this indicates that the binding between the sensor and the metal is 2:1. This 2:1 binding ratio is reasonable. Hg^{2+} generally has a coordination number of four. Nitrogen atom on SAR involved in two of them while chloride (HgCl_2 used in the experiments) occupied other two (Lee et al., 2016). After the metal/sensor ratio was determined, the binding constant was found using a previously reported method (Aydin and Keles 2020b), using absorption values at 528 nm , and it was calculated as $1.56 \times 10^{12} \text{ M}^{-2}$.

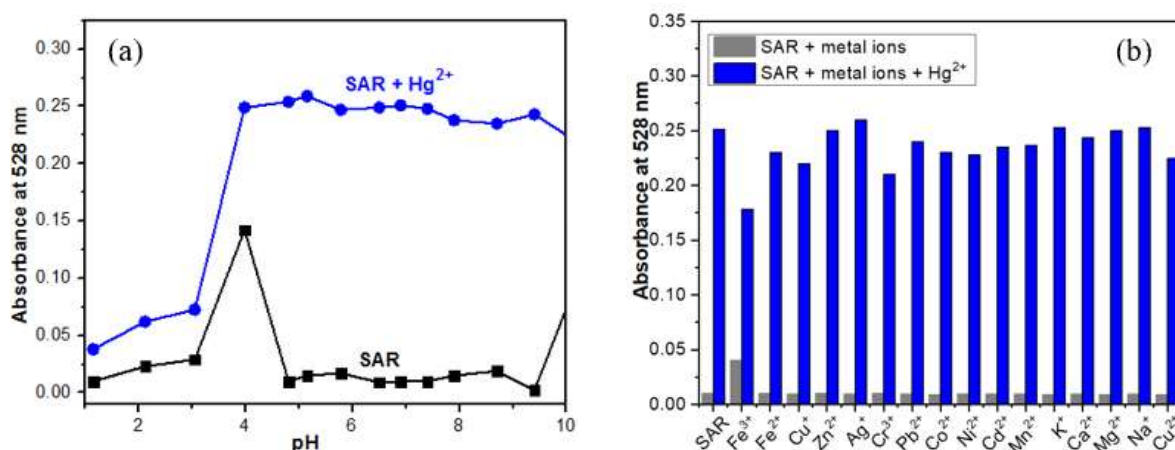


Figure 2. (a) Change of absorption (528 nm) of SAR ($100 \mu\text{M}$) and SAR + Hg^{2+} ($100 \mu\text{M}$) at different pH values in MeOH/ H_2O (v/v, 1:1) (b) Absorption responses of SAR ($100 \mu\text{M}$) to the presence of different metal ions ($200 \mu\text{M}$) (gray bar) followed by the addition of Hg^{2+} (blue bar) in MeOH/ H_2O (v/v, 1:1)

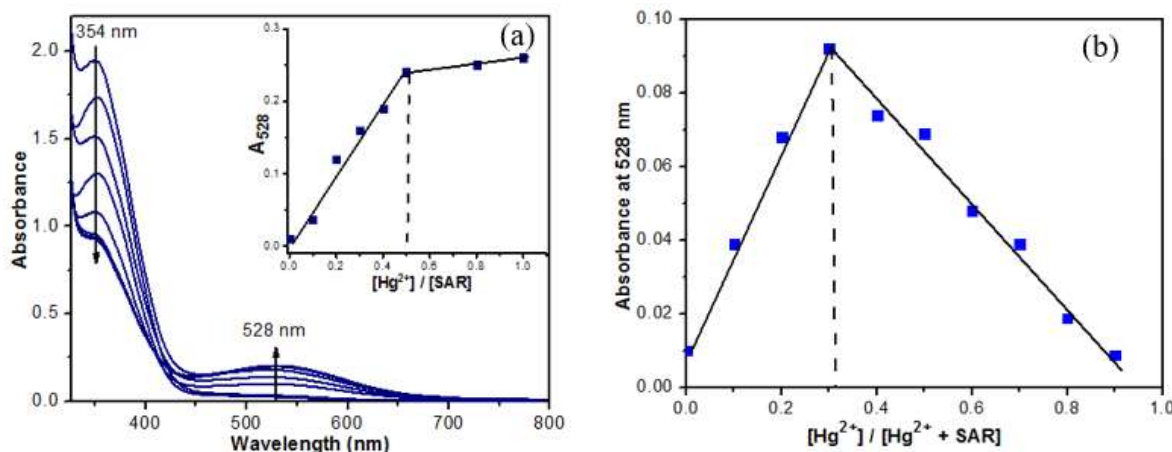


Figure 3. (a) Absorption spectra of SAR ($100 \mu\text{M}$) with the addition of different concentrations of HgCl_2 (0, 10, 20, 30, 40, 50, 75, and $100 \mu\text{M}$, respectively) in MeOH/ H_2O (1:1 v/v). (b) Job's plot

The reversibility of the binding between SAR and Hg^{2+} was also investigated using Na_2S (Aydin et al., 2014). The absorbance peak (528 nm) caused by SAR- Hg^{2+} complex vanished, and the absorbance peak (365 nm) of SAR was reappearance with the addition of Na_2S (Figure 4a). This case also resulted in a color change from pink to yellow. These results suggest that the complex between the sensor and Hg^{2+} is reversible. The possible structure of this process was presented in Scheme 2.

The absorption detection limit of SAR for Hg^{2+} was determined using the results of UV-Vis titration experiments. The absorption intensity of SAR at 528 nm showed good linear increase depending on the concentration of Hg^{2+} ions ranging from 0-50 μM ($R^2 = 0.979$) (Figure 4b). The detection limit for Hg^{2+} was calculated as 7.89 μM . The calculated detection limit is higher than that recommended by WHO; however, it is comparable with the reported values in literature (Lee et al., 2016; Hong et al., 2016).

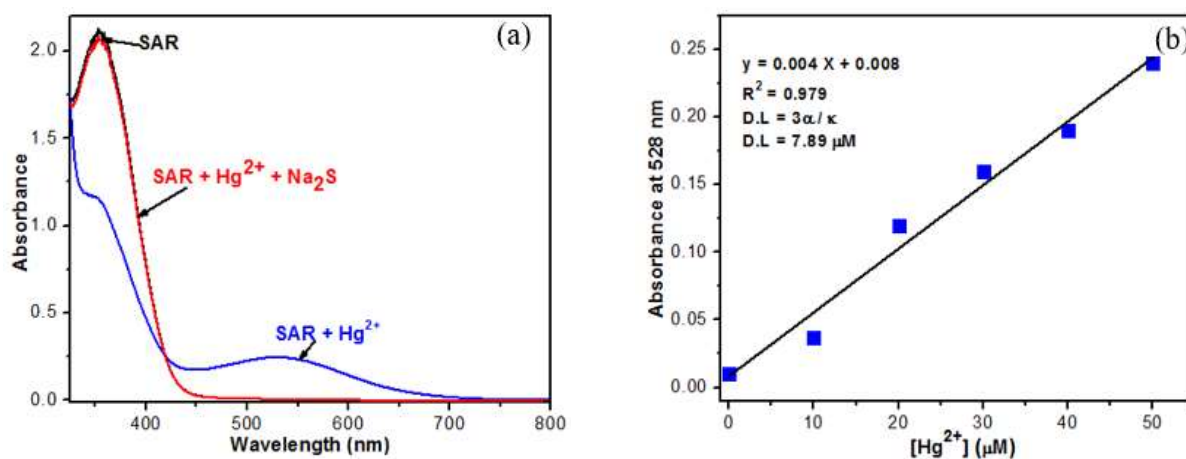
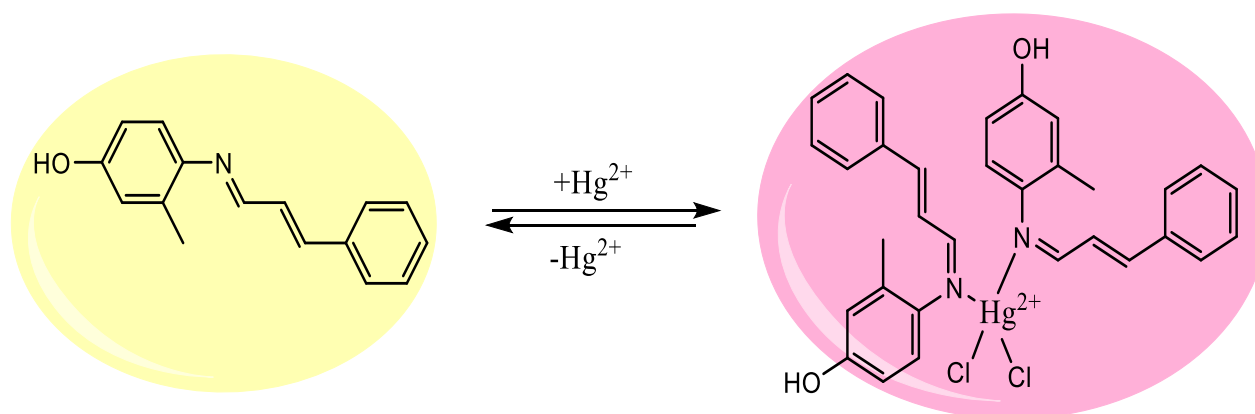


Figure 4. (a) Reversibility of SAR (100 μM) to Hg^{2+} ions by Na_2S . Black line: free SAR (100 μM), blue line: SAR + 1.0 equiv of Hg^{2+} , red line: SAR + 1.0 equiv of Hg^{2+} + 2.0 equiv of Na_2S . (b) Linear relationship between absorbance intensity and Hg^{2+} concentration (0–50 μM) Detection limit of SAR towards Hg^{2+} by UV-Vis method



Scheme 2. Possible reversible binding mode between SAR and Hg^{2+}

CONCLUSION

In this study, a cinnamaldehyde-based compound was investigated as a colorimetric sensor for the detection of metal ions. The results obtained exhibit that SAR has the excellent sensor properties for Hg^{2+} ions in aqueous solutions. Color change response, UV-Vis photo properties, high selectivity, resistance to pH, reversible response, and rapid response time of SAR make it an excellent sensor for the detection of Hg^{2+} ions in aqueous solutions. SAR also has a high binding constant ($1.56 \times 10^{12} \text{M}^{-2}$) and low detection limit (7.89 μM) for Hg^{2+} ions.

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