

## Synthesis of Vanillin-Azine as Colorimetric Chemosensor of Sulfide Anion

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**Abstract:** Vanillin-azine (VA), (4,4'-((1E,1'E)-hydrazine-1,2-diylidenebis(methanelylidene))bis(2-methoxyphenol) has been synthesized from vanillin and tested as anion colorimetric chemosensors for sulfide anion. The VA was obtained from a condensation reaction between vanillin and hydrazine hydrate with a mol ratio of 2:1 mol for 24 h at room temperature. The structure was elucidated using FTIR, GC-MS, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectrometers. The VA compound was examined as a colorimetric chemosensor for sulfide anion over several anions of CN<sup>-</sup>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, N<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>. The structure of the product showed agreement with all spectrometric data. The VA chemosensor tests indicated only selective to S<sup>2-</sup> anion followed by a color change from colorless to light blue in a DMF:HEPES buffer solution (DMF:HBS) medium (9:1, v/v, 10 mM, pH = 7.4). Filter paper strips can detect S<sup>2-</sup> anion with a color change from white to yellow. The VA chemosensor has a limit of detection (LOD) of 5.4 × 10<sup>-4</sup> M, therefore, the VA chemosensor can be applied to detect S<sup>2-</sup> anion in tap water.

**Keywords:** chemosensor; colorimetry; vanillin; vanillin-azine; sulfide anion

### ■ INTRODUCTION

Sulfide anion is one of the toxic anions in the environment because it is corrosive and flammable [1-3]. Prolonged exposure to sulfide ions can cause chronic illnesses, blood disorders, digestive system, respiratory illness, and serious illnesses such as Alzheimer, cancer, diabetes, cardiovascular diseases [3-4], and Down's syndrome [5]. Due to the impacts caused by the presence of sulfide anions in the environment, it is necessary to detect and monitor the sulfide ions, especially in sectors close to the human environment.

Sulfide anion can be detected by ion chromatography [6], electrochemical [7], and potentiometry methods [8]. However, these methods need time-consuming sample preparation and are not easy to operate. Therefore, developing simple, efficient, and faster techniques is necessary. The color change can be used to detect anions using colorimetric chemosensors [9]. The methods provide a qualitative and quantitative analysis directly with the naked eye [10-11]. The detection with colorimetric chemosensors is simpler, selective, inexpensive, rapid, and sensitive [12-13]. The

colorimetric chemosensors consist of a bonding side for chemical, electrostatic, or hydrogen bonding interactions and a signal side that provides the color change information [14-15]. The sulfide chemosensors provide quick and selective detection and have been studied by many researchers. Mechanism of detections has been reported via nucleophilic reactions [16-17], formation of amines from azides reduction [18], and sulfide displacement to metal ions [19-20]. The deprotonation mechanism has also been reported for colorimetric sulfide chemosensors. Chemosensors contain binding sides of -OH and chromophore group side of azine (-C=N-N=C-) as the signal side have been reported [21]. Azine derivatives with a phenolic group can detect sulfide anions by giving color changes [1]. One source of phenols is vanillin, where the phenolic group can be used as a binding site, and the aldehyde group can be developed as a signal site.

In this study, we would like to report the synthesis of azine derivative from vanillin and investigate its performance as a colorimetric chemosensor for sulfide anion along with various sensing properties such as

anion selectivity and interference, time interaction, pH effect, sensitivity, as well as reversibility. Furthermore, a filter paper strip for a qualitative test of sulfide anion has also been visualized, while quantitative analysis of sulfide anion in tap water sample shows an application of vanillin-azine as a sulfide anion chemosensor.

## ■ EXPERIMENTAL SECTION

### Materials

All of the materials such as vanillin, hydrazine hydrate, and sodium salt of the anions are purchased from E Merck. Solvents were used without further purification. In addition, the HEPES Buffer Solution (HBS) pH 7.4 was prepared in deionized water.

### Instrumentation

The absorption spectra were obtained from a UV-Vis spectrophotometer (Shimadzu UV-1800). The IR spectra were recorded from an infrared spectrophotometer (Shimadzu Prestige-21). The mass spectra were done by Gas Chromatography-Mass Spectrometer (Shimadzu QP-2010S). The  $^{13}\text{C}$ -NMR spectra analysis was done by Agilent 125 MHz, while the  $^1\text{H}$ -NMR spectra analysis was performed with Agilent 500 MHz.  $\text{DMSO}-d_6$  was used for the NMR solvent.

### Procedure

#### **Synthesis of vanillin-azine (VA)**

Vanillin-azine (VA) was synthesized based on the modification procedures of previous research [22-23]. Vanillin (20 mmol, 3.04 g) was dissolved in ethanol (10 mL), and then 0.6 mL (10 mmol) of hydrazine hydrate 80% was added dropwise. The reaction was stirred at room temperature for 24 h. Then, cooled distilled water was added to the solution, and the mixture was stirred for 30 min. The mixture was kept for several minutes. The yellow solid was filtered, washed with cold ethanol, and then dried for recrystallization. The pale-yellow crystal was obtained in 86% yield (m.p. 178–179 °C, Lit. 181 °C [23]). FTIR (KBr  $\text{cm}^{-1}$ ): 3475 (O-H), 3066 (C-H aromatic), 2928 (C-H alkane), 1598 (C=N imine), 1457 (C=C aromatic), and 1262 (C-O-C ether).  $^1\text{H}$ -NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 3.82 (s, 3H,  $-\text{OCH}_3$ ), 6.86 (d,  $J = 8.1$  Hz, 1H, Ar), 7.24 (dd,  $J = 8.15$  Hz, 1.85 Hz, 1H, Ar),

7.45 (d,  $J = 1.9$  Hz, 1H, Ar), 8.57 (s, 1H,  $-\text{CH}=\text{N}-$ ), and 9.69 (s, H,  $-\text{OH}$ );  $^{13}\text{C}$ -NMR (125 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  (ppm) = 160.64, 147.99, 110.03, 125.55, 123.52, 115.51, 149.89, and 55.53. GCMS ( $m/z$ ) = 300.

#### **Solvatochromic study of VA chemosensor**

For the solvatochromic study, the VA was dissolved in dimethylformamide, dimethylsulfoxide, acetonitrile, dichloromethane, and a solvent mixture of DMF:HEPES Buffer Solution (HBS) (9:1, v/v, 10 mM, pH 7.4) to give the concentration of  $1 \times 10^{-3}$  M. Solution color was observed, and the maximum wavelength was measured with UV-Vis spectrophotometer at a concentration of  $2 \times 10^{-5}$  M.

#### **Selectivity study of VA chemosensor with different anions**

The VA chemosensor ( $2 \times 10^{-5}$  M) solution was prepared in DMF:HBS solvent (9:1, v/v, 10  $\mu\text{M}$ , pH 7.4). The solution of anions (0.2 M), including  $\text{S}^{2-}$ ,  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{NO}_3^{2-}$  was prepared in HBS. The solution (100  $\mu\text{L}$ ) was added to 3.9 mL of VA solution. The color change of the VA solutions was observed, and the maximum wavelength was then measured using a UV-Vis spectrophotometer.

#### **Competitive study of VA chemosensor with different anions and $\text{S}^{2-}$**

For the competitive study, the solution of VA ( $2 \times 10^{-5}$  M) was prepared in DMF:HBS (9:1, v/v, 10  $\mu\text{M}$ , pH 7.4). The anion solution of  $\text{S}^{2-}$ ,  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{NO}_3^{2-}$  (0.2 M) were prepared in HBS. Solution of  $\text{CN}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ ,  $\text{CH}_3\text{COO}^-$ , and  $\text{NO}_3^{2-}$  (100  $\mu\text{L}$ ) was added to VA solution (3.9 mL), and then  $\text{S}^{2-}$  anion (100  $\mu\text{L}$ ) was added to the mixture of VA-anion solution. The color change was recorded, and the maximum wavelength was measured with a UV-Vis spectrophotometer.

#### **Time-dependent study**

The VA chemosensor solution ( $2 \times 10^{-5}$  M) was prepared in DMF:HBS solvent (9:1, v/v, 10  $\mu\text{M}$ , pH 7.4). The  $\text{S}^{2-}$  anion solution (0.2 M, 100  $\mu\text{L}$ ) was added to 3.9 mL of VA solution. The absorbance was monitored using a UV-Vis spectrometer with different time intervals at room temperature.

### The limit of detection (LOD) of VA towards S<sup>2-</sup>

The VA solution ( $2 \times 10^{-5}$  M) in DMF:HBS (9:1, v/v, 10  $\mu$ M, pH 7.4) and S<sup>2-</sup> anion solution (0.2 M) from Na<sub>2</sub>S in HBS were prepared. The S<sup>2-</sup> anion solution with various volumes of 20–100  $\mu$ L (1–5 mM) was added to 3.9 mL of VA solution. The color change was recorded, and absorbance was measured using a UV-Vis spectrophotometer. The data obtained were used to make a calibration curve of S<sup>2-</sup> concentration vs absorbance. The limit of detection was determined using Eq. 1 [24].

$$\text{LOD} = \frac{3 (\text{standard deviation})}{\text{slope}} \quad (1)$$

### Reusability study of VA

For the reusability study, 3 mL of VA solution ( $2 \times 10^{-5}$  M) in DMF:HBS (9:1, v/v, 10  $\mu$ M, pH 7.4) was treated with 87  $\mu$ L of S<sup>2-</sup> anion solution (0.2 M) in HEPES Buffer Solution. The absorbance was measured then followed by the HCl addition (2 M, 17  $\mu$ L) in the HEPES Buffer Solution. The UV-Vis absorption was monitored at a wavelength of 614 nm. For the next run, the addition of S<sup>2-</sup> and HCl was performed until the solution became saturated.

### pH-dependent study of VA chemosensor

The VA solution ( $2 \times 10^{-5}$  M) was prepared in DMF:HBS with various pH of 3, 5, 7.4, 9, and 11. The pH was adjusted using HCl and/or NaOH solution. Then, the sulfide anion solution (0.2 M, 100  $\mu$ L) in HEPES Buffer Solution was added to the vial. The color change was recorded, and the UV-Vis absorbance was monitored before and after the addition of the S<sup>2-</sup> anion.

### Filter paper strip study of VA chemosensor

Filter paper strip study was carried out by immersing Whatman No.42 filter paper in the VA ( $1 \times 10^{-3}$  M) solution prepared in DMF:HBS (9:1, v/v, 10  $\mu$ M, pH 7.4) for 2 h. The paper was then dried in an oven overnight. The test was conducted by dropping several

drops of S<sup>2-</sup> anion solution to filter paper strips with various concentrations of 0.01, 0.1, 0.2, and 1 M. The color change of the filter paper strips sensor was observed directly by the naked eye.

### Application of VA chemosensor for the analysis of S<sup>2-</sup> anion in tap water

Samples of tap water from two different sampling sources and VA solution ( $2 \times 10^{-5}$  M) in DMF:HBS (9:1, v/v, 10  $\mu$ M, pH 7.4) solvent were prepared. Then, the tap water samples were added by S<sup>2-</sup> anion solutions to 1, 3, and 5 mM, respectively. The color change was observed and analyzed using UV-Vis spectrophotometry at 614 nm wavelength and determined the recovery of each tap water sample.

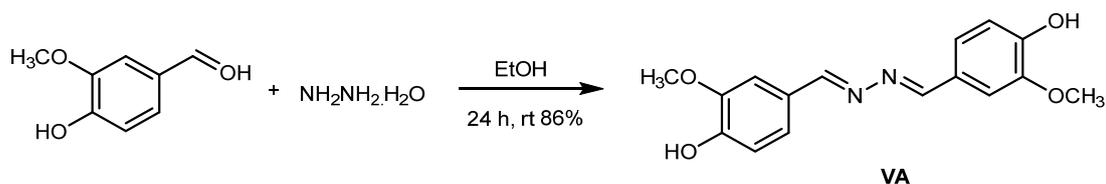
### <sup>1</sup>H-NMR titration studies

The mixture of VA compound and Na<sub>2</sub>S was prepared with a concentration ratio of 1:1 (0.03 M:0.03 M) and 1:2 (0.03 M:0.06 M). The VA was dissolved in DMSO-*d*<sub>6</sub>, while Na<sub>2</sub>S was dissolved in D<sub>2</sub>O solvent. The <sup>1</sup>H-NMR titration analysis was carried out after the reaction between the VA chemosensor and Na<sub>2</sub>S for  $\pm$ 18 min.

## RESULTS AND DISCUSSION

### Synthesis of Vanillin-Azine (VA)

The VA compound was synthesized through a condensation reaction from vanillin and hydrazine hydrate (mol ratio of 2:1) in ethanol at room temperature for 24 h (Scheme 1). The crude product was recrystallized from a mixture of ethanol and distilled water to give a pale-yellow solid with m.p. of 178–179 °C (close to the literature, i.e., 181 °C) [23]. The formation of vanillin-azine was confirmed by the FTIR spectrum, indicating the loss of absorption peak of the carbonyl group (C=O) at 1666 cm<sup>-1</sup> and the appearance of new absorption of the imine group (C=N) at 1598 cm<sup>-1</sup>. The



Scheme 1. Synthesis of VA

$^1\text{H-NMR}$  spectra showed the formation of the imine group ( $-\text{CH}=\text{N}-$ ) at  $\delta$  8.57 ppm as a singlet for 1H.

### Solvatochromic Study of VA Sensor

For the solvatochromic studies, the VA compound was dissolved in DMF, DMSO, DCM, acetonitrile, and a mixed solvent of DMF:HBS (9:1, v/v, 10 mM, pH = 7.4). The VA compound has good solubility in all solvents ( $2 \times 10^{-5}$  M), and no color occurs (colorless), as shown in Fig. 1(a). Based on UV-Vis spectra in Fig. 1(b), the VA solution in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4), DMF, and DMSO give one peak at  $\lambda_{\text{max}}$  351, 352, and 354 nm, respectively. While in DCM and acetonitrile, the absorption peak is observed at  $\lambda_{\text{max}}$  of 342 and 341 nm. The results show that the solvent with higher polarizability ( $\pi^*$ ) gives higher  $\lambda_{\text{max}}$  [25].

### Selectivity Study of Sensor VA with Different Anions

The selectivity study was carried out by observing the color change using the naked eye and measuring the absorbance of UV-Vis spectra after the addition of various

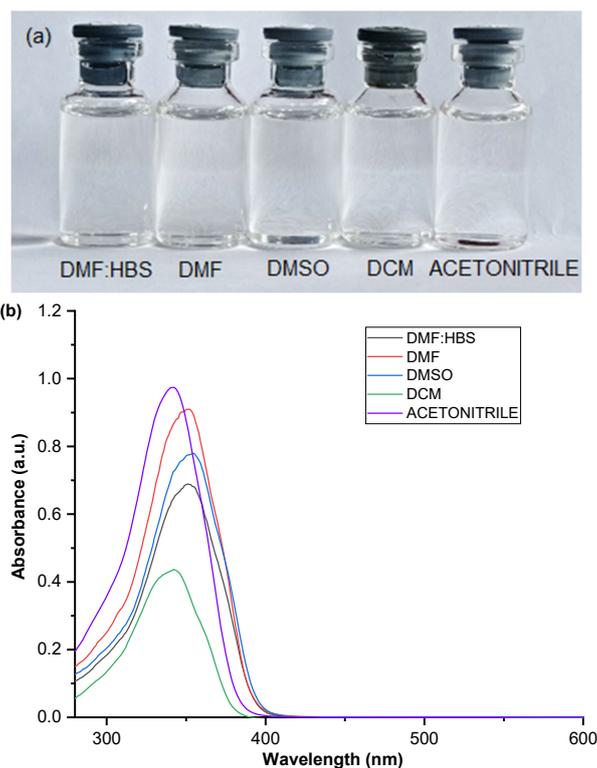


Fig 1. (a) VA chemosensor solution b) UV-Vis spectra of VA solution ( $2 \times 10^{-5}$  M) in various solvent

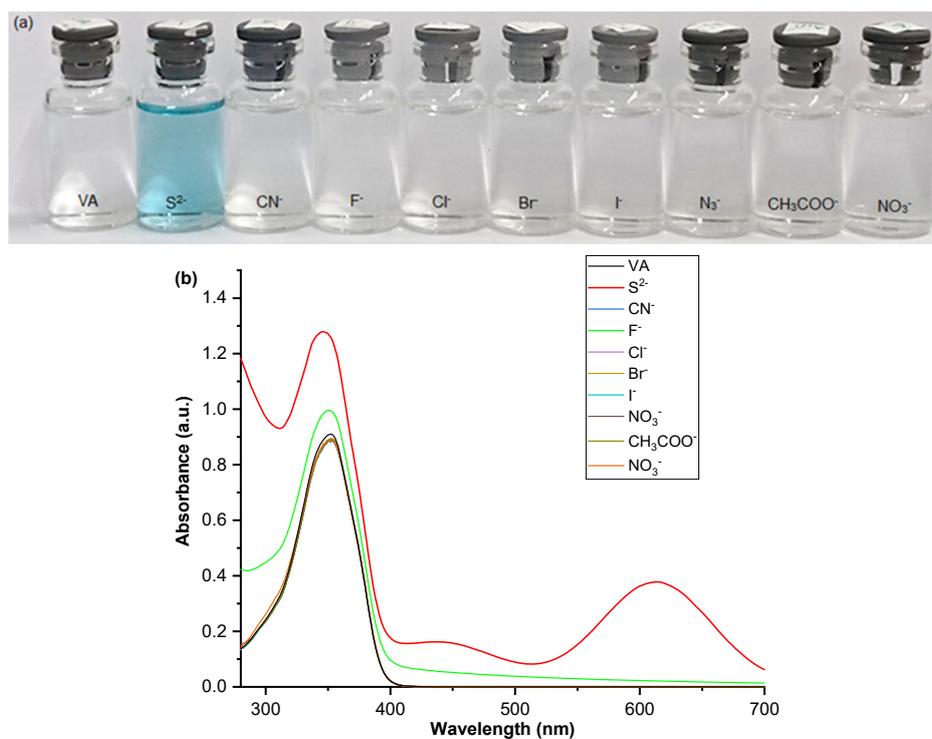


Fig 2. (a) The color of VA chemosensor solution, (b) UV-Vis spectra of VA chemosensor after the addition of various anions

anions, such as  $S^{2-}$ ,  $CN^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $N_3^-$ ,  $CH_3COO^-$  and  $NO_3^{2-}$  into VA solution in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4) Based on Fig. 2(a), the VA compound shows the selectivity to detect  $S^{2-}$  anion by the color change from colorless to light blue. The color change was supported by UV-Vis spectra in Fig. 2(b), showing the absorbance at 614, 450, and 351 nm after the addition of  $S^{2-}$ . In the presence of  $S^{2-}$  anion, a bathochromic shift was observed until 263 nm. The shift occurs due to the interaction between the VA chemosensor and  $S^{2-}$  anion through a Brønsted-Lowry acid-base interaction. After deprotonation of the phenolic group, the electron delocalization occurs towards the  $-C=N-N=C-$  group.

### Competitive Study of Sensor VA with Different Anions and $S^{2-}$

In this study, each vial contains a VA solution and one of the anions ( $CN^-$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $N_3^-$ ,  $CH_3COO^-$ ,  $NO_3^{2-}$ ) as the competing anion. Then, the  $S^{2-}$  anion was added to study the interference. The color change from

colorless to light blue was observed except for  $CN^-$  anion (Fig. 3). It should be noted that there is no significant interference observed in the presence of  $F^-$  anion, although the  $F^-$  anion is known as a good anion to deprotonate the phenols in some chemosensor compounds. The interference occurred in the presence of  $S^{2-}$  and  $CN^-$  anions giving color change from colorless to pale yellow. The UV-Vis spectra confirmed those cases in Fig. 4(a) and 4(b). These results confirm that the VA chemosensor can detect  $S^{2-}$  anions in the presence of other anions except  $CN^-$ .

### Time-Dependent Study

The time-dependent study was carried out by adding 100  $\mu$ L of sulfide anion to VA solution in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4). The absorbance of the solution was then monitored at 614 nm for 30 min. This study was done to know how fast the chemosensor responds in detecting sulfide analytes. Fig. 5 represents that the absorbance increment is detected in the first



Fig 3. The color change due to the competition between  $S^{2-}$  and other anions

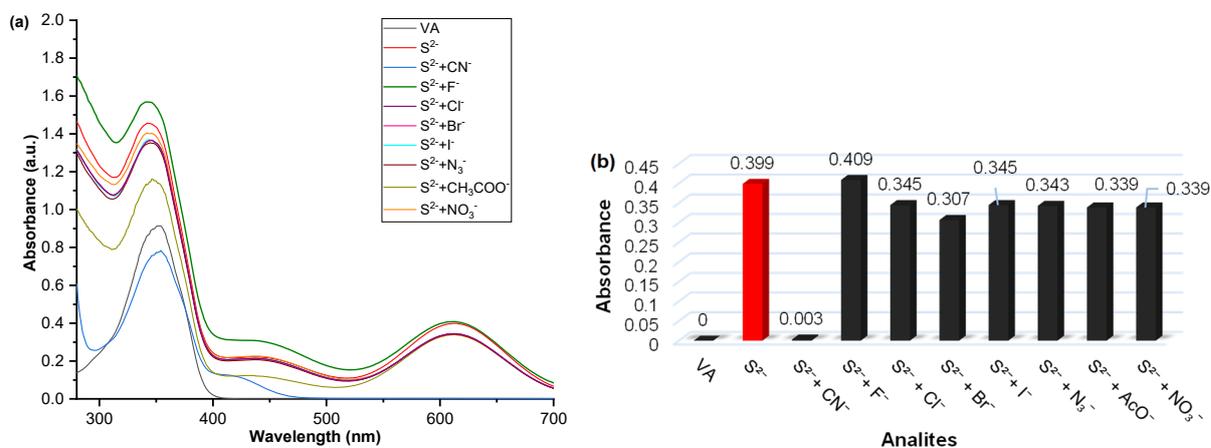


Fig 4. (a) UV-Vis spectra (b) Bar diagram of the competitive studies of VA chemosensor towards  $S^{2-}$  in the presence of other anions

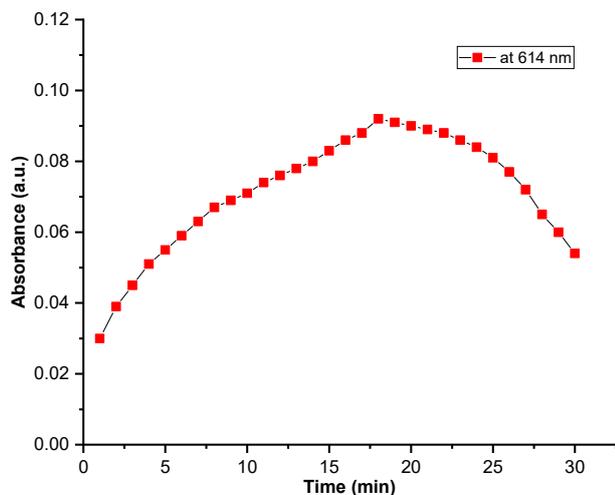


Fig 5. Time-dependent study of VA chemosensor with  $S^{2-}$

minute and kept increasing up to 18 min. From the 19<sup>th</sup> min to the 30<sup>th</sup> min, the absorbance decreased. This study also confirms that the VA chemosensor compound could respond to sulfide anion in less than 1 min and reach the maximum absorbance in 18 min of interaction.

#### Limit of Detection (LOD) of Sensor VA towards $S^{2-}$

Fig. 6 shows the color change of the VA chemosensor after the addition of sulfide anion solution



Fig 6. The color change of VA chemosensor ( $2 \times 10^{-5}$  M) after the addition of  $S^{2-}$  anion solution at various concentrations

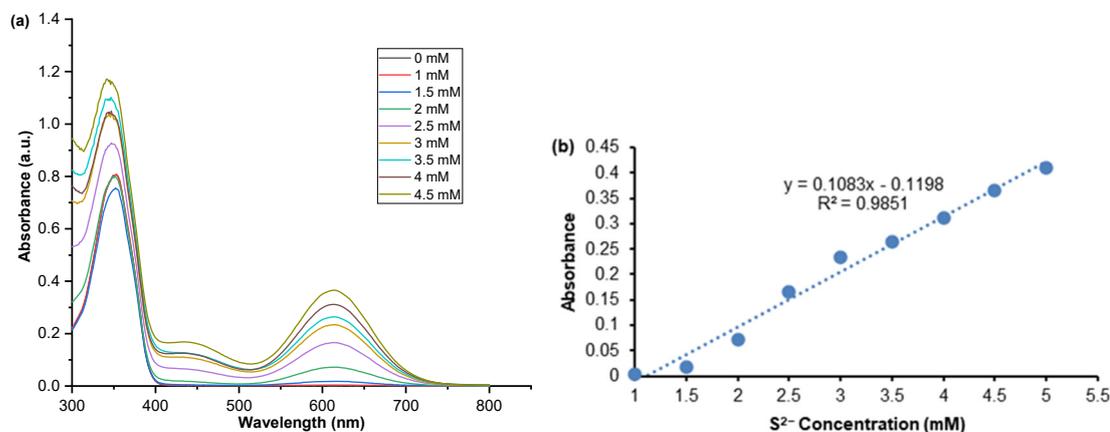


Fig 7. (a) UV-Vis spectra of VA after the addition of  $S^{2-}$ , (b) calibration curve of  $S^{2-}$  at various mM concentrations at 614 nm

at various concentrations. At the concentration of 1.5 mM, the color of the solution is changed from colorless to light blue. The intensity of the blue color is getting stronger with the increase of  $S^{2-}$  concentration.

The color change was also confirmed using UV-Vis spectra (Fig. 7(a)). The measurement of absorbance was carried out at 614 nm at 18 min of interaction. By using the linear regression equation of the calibration curve, the LOD was calculated using Eq. (1). The coefficient correlation ( $R^2$ ) of the calibration curve for various  $S^{2-}$  concentrations is 0.9851, and the LOD of the VA chemosensor is  $5.4 \times 10^{-4}$  M.

#### Reusability Study of VA Chemosensor

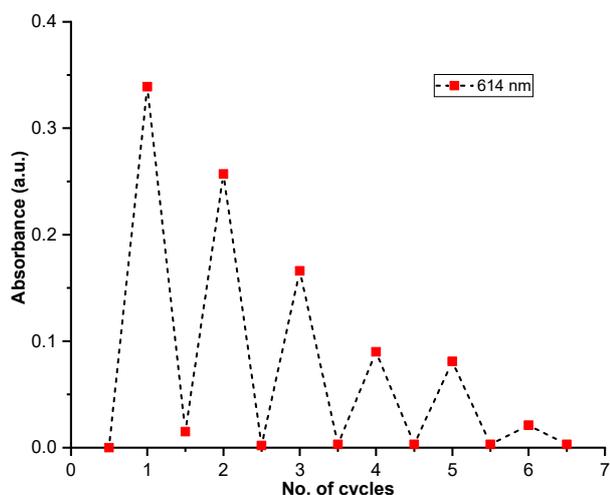
The reusability study was carried out to determine the chemosensor's ability to reuse after interaction with an analyte. When VA interacted with  $S^{2-}$  anion analyte, VA became a deprotonated structure and produced blue color. Then, the addition of HCl solution (2 M) protonated the deprotonated structure of VA to become a neutral VA structure, along with color change from blue to colorless. In the experiment, a solution of VA ( $2 \times 10^{-5}$  M) was treated with  $S^{2-}$  (87  $\mu$ L, 0.2 M) and then

followed by protonation using HCl solution (17  $\mu\text{L}$ , 2 M) each time alternatively. The color change was observed by spectral changes at 614 nm. In the first cycle, the absorbance will increase after the addition of  $\text{S}^{2-}$  anion, and then absorbance will lose after protonation with HCl. The color and spectrum change showed the reusability of VA solution for  $\text{S}^{2-}$  anion detection at least for five cycles (Fig. 8).

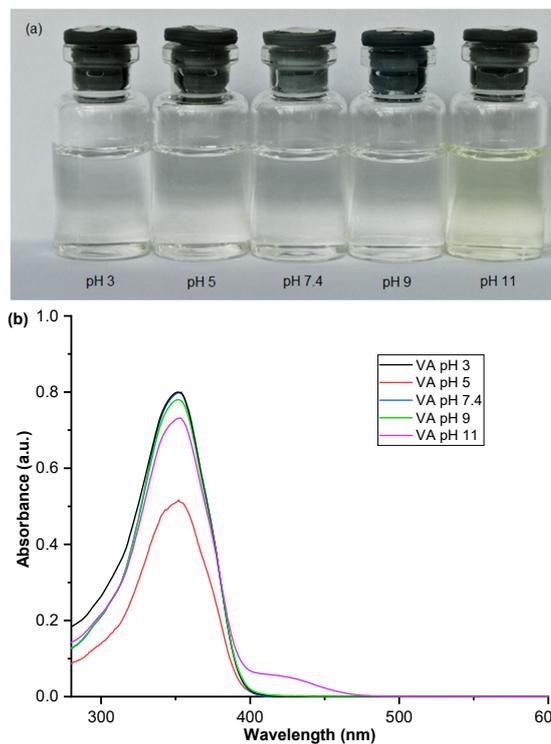
### pH-Dependent Study of VA Chemosensor

In this study, the VA compound ( $2 \times 10^{-5}$  M) was dissolved in DMF:HBS (9:1, v/v, 10 mM) with various pH. The variation of pH buffer was 3, 5, 7.4, 9, and 11. Fig. 9(a) shows the color of the VA solution before the addition of the  $\text{S}^{2-}$  anion. At pH 11, the sensor solution gives a light yellow color. The UV-Vis spectra at pH 11 show the absorbance in the visible area at 435 nm (Fig 9(b)).

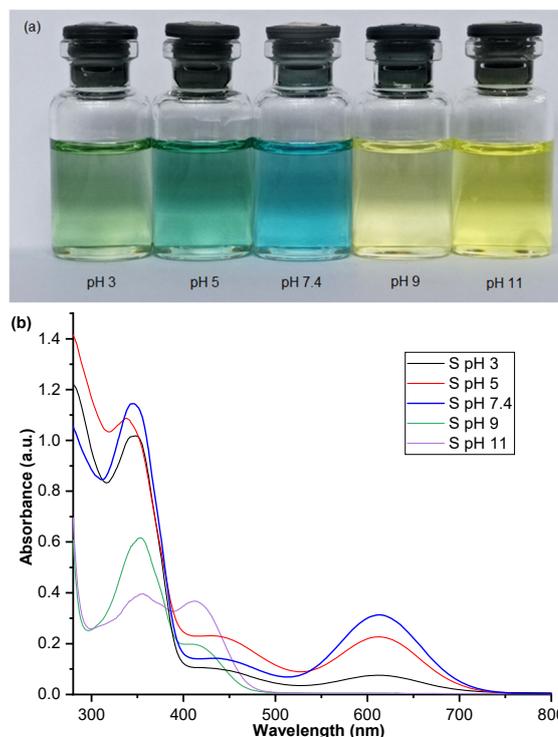
Color of the VA solution changes after the addition of the  $\text{S}^{2-}$  solution (100  $\mu\text{L}$ ) at all pH (Fig. 10(a)). The color change was confirmed by UV-Vis spectra (Fig. 10(b)). At pH 3, 5, and 7.4, the UV-Vis spectra have the same maximum wavelength of 614 nm but different absorbance intensities. At pH 9 and 11, the UV-Vis spectra have absorption at 412 nm. We can conclude that the interaction between VA chemosensor and  $\text{S}^{2-}$  anion can be detected by colorimetry at a pH of 3–7.4, where pH 7.4 is the optimum pH for the VA compound to detect  $\text{S}^{2-}$  anion. In the solvent of DMF:HBS,  $\text{Na}_2\text{S}$  interacts with  $\text{H}_2\text{O}$  from the buffer solution and dissociates into  $\text{Na}^+$ ,  $\text{H}^+$ ,



**Fig 8.** Reusability study of VA chemosensor ( $2 \times 10^{-5}$  M) with  $\text{S}^{2-}$  (0.2 M, 87  $\mu\text{L}$ )



**Fig 9.** (a) The color of VA solution and (b) UV-Vis spectra of VA chemosensor at various pH



**Fig 10.** (a) The color change of VA solution and (b) The UV-Vis spectra of VA chemosensor after the addition of  $\text{S}^{2-}$  anion

$\text{HS}^-$ , and  $\text{S}^{2-}$ . The sulfide anion in water will be in the form of  $\text{H}_2\text{S}/\text{HS}^-$  species at a pH of 3–7.4, while in the base solution, the sulfide anion will be in the form of  $\text{HS}/\text{S}^{2-}$  [26]. In this manuscript,  $\text{S}^{2-}$  anion will refer to the mixture of  $\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$  as same as the Kaushik report [1].

### Filter Paper Strips Studies of VA Chemosensor

One of the qualitative tests to determine  $\text{S}^{2-}$  anion was carried out by filter paper strip consisting of VA compound [27]. The Whatman No.42, with a size of  $1 \times 3$  cm, was immobilized with a VA compound ( $1 \times 10^{-3}$  M) in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4), then the  $\text{S}^{2-}$  anion solution was added with various concentrations of 0.01, 0.1, 0.2, and 1 M. Fig. 11 shows the color change of filter paper strips from white to yellow at 0.1, 0.2, and 1 M of  $\text{S}^{2-}$  solution. The color change indicates a positive response from the VA compound in the presence of  $\text{S}^{2-}$  anion. Based on this test, it can be concluded that the VA compound is able to qualitatively detect the  $\text{S}^{2-}$  anion with filter paper strips.

### Application of VA Chemosensor in the Analysis of $\text{S}^{2-}$ Anion in Tap Water

For the quantitative analysis of sulfide in water samples, the samples of tap water were added to  $\text{S}^{2-}$  anion solution until concentrations of 1, 3, and 5 mM. Then, the VA compound solution ( $2 \times 10^{-5}$  M) in DMF:HBS (9:1, v/v, 10 mM, pH = 7.4) was added to tap water samples, as shown in Table 1. The results show that the VA chemosensor is able to detect  $\text{S}^{2-}$  anion with a satisfactory

value of RSD and recovery. Based on this data, it can be concluded that the VA chemosensor has good precision and accuracy for detecting  $\text{S}^{2-}$  anions at various concentrations of 1, 3, and 5 mM.

### $^1\text{H-NMR}$ Titration Study for Interaction Mechanism of VA- $\text{S}^{2-}$

Color change after the addition of  $\text{S}^{2-}$  anion to VA solution was predicted involving the deprotonation of a phenolic group with  $\text{S}^{2-}$  anion, as shown in Scheme 2.

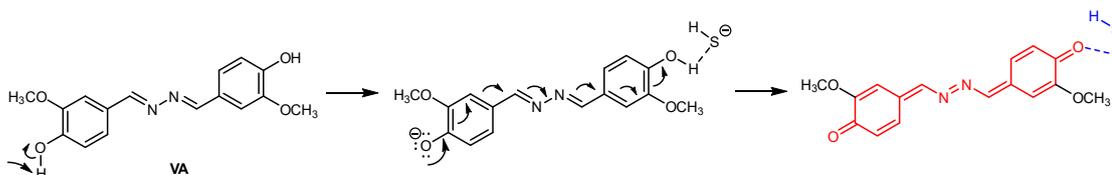
This mechanism of VA and  $\text{S}^{2-}$  anion was confirmed by the  $^1\text{H-NMR}$  titration test. The -OH peak of VA at 9.69 ppm disappeared after the addition of 1 and 2 mol equivalent of  $\text{S}^{2-}$  anion solution (Fig. 12). In addition, this process leads to the shift of the rest of the proton peaks towards the up-field [1]. This is because the deprotonation of the -OH is followed by the delocalization process. Based on Fig. 12, the VA has been



**Fig 11.** The color change of VA immobilized paper strips in the presence of  $\text{S}^{2-}$  anion at various concentration

**Table 1.** Determination of  $\text{S}^{2-}$  anion in water samples

Samples	$\text{Na}_2\text{S}$ added (mM)	$\text{Na}_2\text{S}$ found (mM)	Recovery (%)	RSD (%)
Tap Water	-	-	-	-
1	1	$1.12 \pm 0.005$	112.77	0.47
2	3	$3.06 \pm 0.037$	102.12	1.21
3	5	$4.63 \pm 0.074$	92.79	1.60



**Scheme 2.** The interaction mechanism of VA chemosensor with  $\text{S}^{2-}$  anion

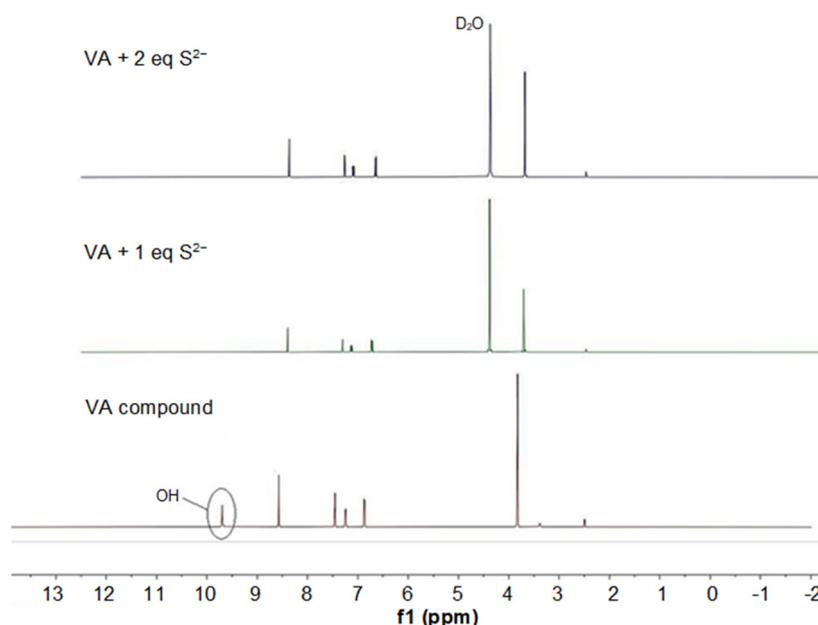


Fig 12.  $^1\text{H-NMR}$  titration of the VA chemosensor with the addition of  $\text{S}^{2-}$  anion solution (1 and 2 Eq.)

deprotonated by 1 mol equivalent of  $\text{Na}_2\text{S}$  solution. Therefore, the interaction of VA with  $\text{S}^{2-}$  could be predicted by a 1:1 ratio. When one phenolic proton is deprotonated, another -OH peak does not appear in the  $^1\text{H-NMR}$  spectra because it is converted to -OD form in  $\text{D}_2\text{O}$  solvent.

## CONCLUSION

The azine derivative (VA) was synthesized as a sulfide anion colorimetric chemosensor with a yield of 86.3%. The VA chemosensor was selective for the  $\text{S}^{2-}$  anion and followed a color change from colorless to light blue. Test paper of VA indicated color changes from white to yellow with different concentrations of  $\text{S}^{2-}$  anion. The limit of detection (LOD) of the VA chemosensor is  $5.4 \times 10^{-4}$  M. The VA chemosensor could be used to detect  $\text{S}^{2-}$  anion in tap water samples.

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