# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Preliminary study of the naked eye detection of arsenic

The $BF_2$-curcumin dissolved in 60% ethanol displayed an orange solution with the maximum absorbance at 509 nm. In the presence of As(III), the color of $BF_2$-curcumin turned to blue and the maximum absorbance shifted to a longer wavelength that could be measured by visible spectrophotometer at 632 nm (Figure 4.1). This change of color can be ascribed to the change of $BF_2$-curcumin molecular structure. The $BF_2$-curcumin consists of two methoxy phenol groups as electron donor parts conjugated to the difluoroboron enolate as the electron acceptor part (Figure 2.7). Because As(III) in water is normally present in oxyanion form and its acid dissociation constants were quite low ($pKa_1$=9.2, $pKa_2$=12.1 and $pKa_3$=12.7) [5, 21], arsenite ion can presumably deprotonate the hydroxyl moiety of $BF_2$-curcumin molecule and the negative charges produced could delocalize to an acceptor part, as depicted in Figure 2.8, which resulted in such change of color and absorption wavelength.

Moreover, in the presence of As(V), the color of $BF_2$-curcumin similarly turned to blue like As(III) but with relatively lower absorption at 632 nm (Figure 4.1). In terms of naked eye detection, the change in color of $BF_2$-curcumin with As(III) solution was more clearly observed when comparing with $BF_2$-curcumin with As(V) solution (Figure 4.2). Thus, due to higher sensitivity (higher absorbance for As(III) with the concentration of As(III) and As(V)) the colorimetric method by using $BF_2$-curcumin was clearly favorable for the determination of As(III).

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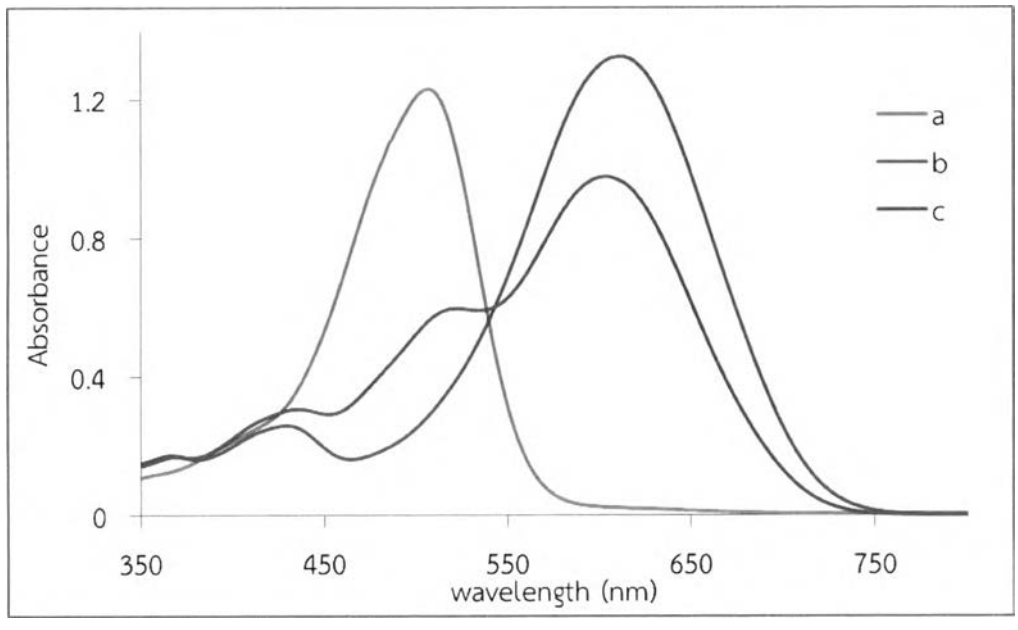


**Figure 4.1** The UV-visible spectra of (a) $BF_2$-curcumin solution, (b) in the presence of 100 μM of As(III) and (c) in the presence of 100 μM of As(V).

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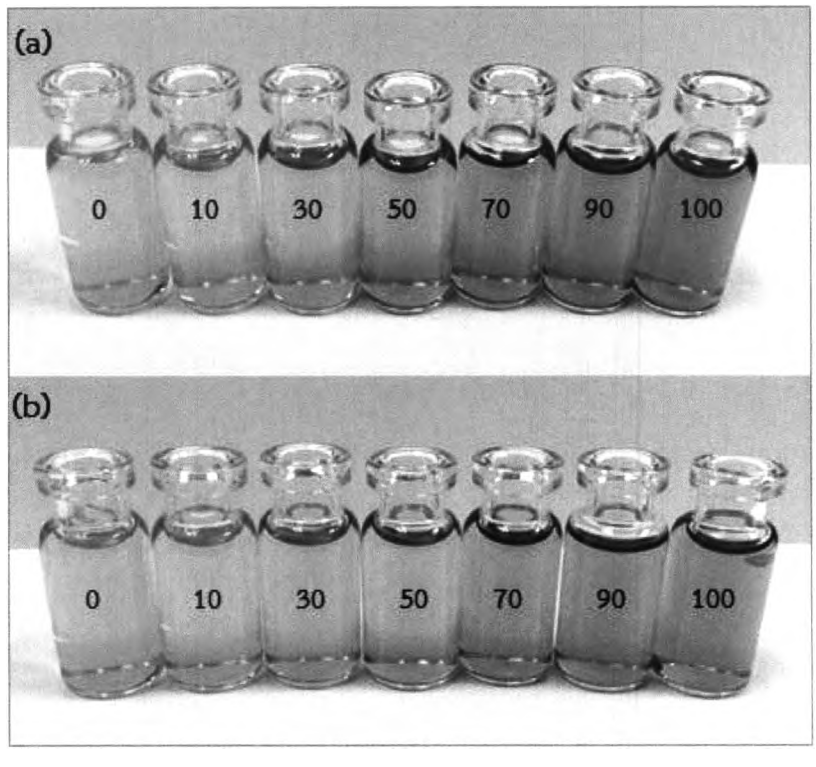


**Figure 4.2** The color of $BF_2$-curcumin solutions in presence of 0-100 μM of (a) As(III) and (b) As(V) solution.

## 4.2 Colorimetric and naked eye detections of arsenic in solution system

### 4.2.1 Effect of concentration of $BF_2$-curcumin solution

The concentrations of $BF_2$-curcumin solution were varied in the range of 5-30 μM in the presence of different As(III) concentrations from 0-200 μM. Figure 4.3 showed the plot between concentration of As(III) solution and absorbance at 632 nm of $BF_2$-curcumin in various concentrations. It was found that when the concentration of $BF_2$-curcumin was lower than 20 μM, the absorbance at 632 nm increased with increasing concentration of As(III), however, the sensitivity was significantly low. On the other hand, the experiment using the concentration of $BF_2$-curcumin above 20 μM showed higher sensitivity yet the linear range was narrower. As the toxicity of As(III) can occur at relatively low levels, the sensitivity of method is given priority over its quantitative range and thus the $BF_2$-curcumin concentration of 20 μM was chosen for all further colorimetric experiments.

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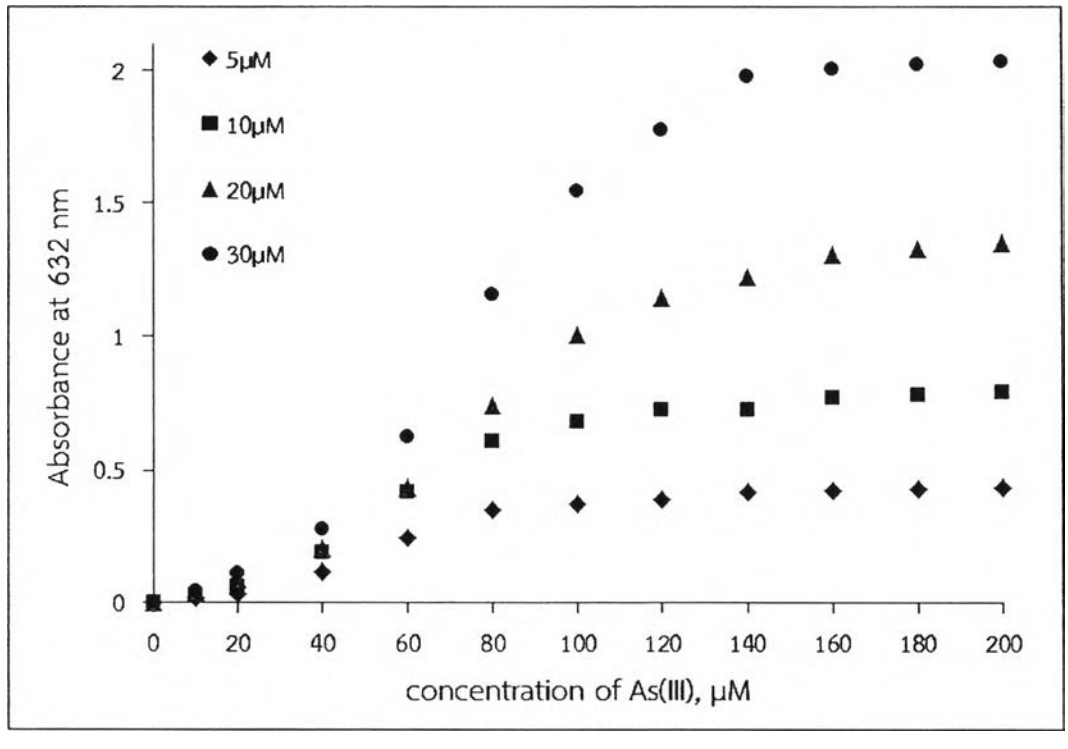


**Figure 4.3** The effect of the concentration of $BF_2$-curcumin in various concentration of As(III) from 0-200 μM.

Regarding the naked eye detection, the concentrations of $BF_2$-curcumin solution were varied in the range of 5 to 30 μM in the presence of different As(III) concentrations from 0 to 100 μM. The changes of solution color from orange to blue were clearly correlated with varying concentrations of As(III). The photograph of the $BF_2$-curcumin solutions with As(III) in various concentration was shown in Figure 4.4. This observation suggested that the 10 μM $BF_2$-curcumin solution exhibited the color which could be clearly and easily differentiated with increasing concentration of As(III), therefore it was selected as a model for naked eye detection.

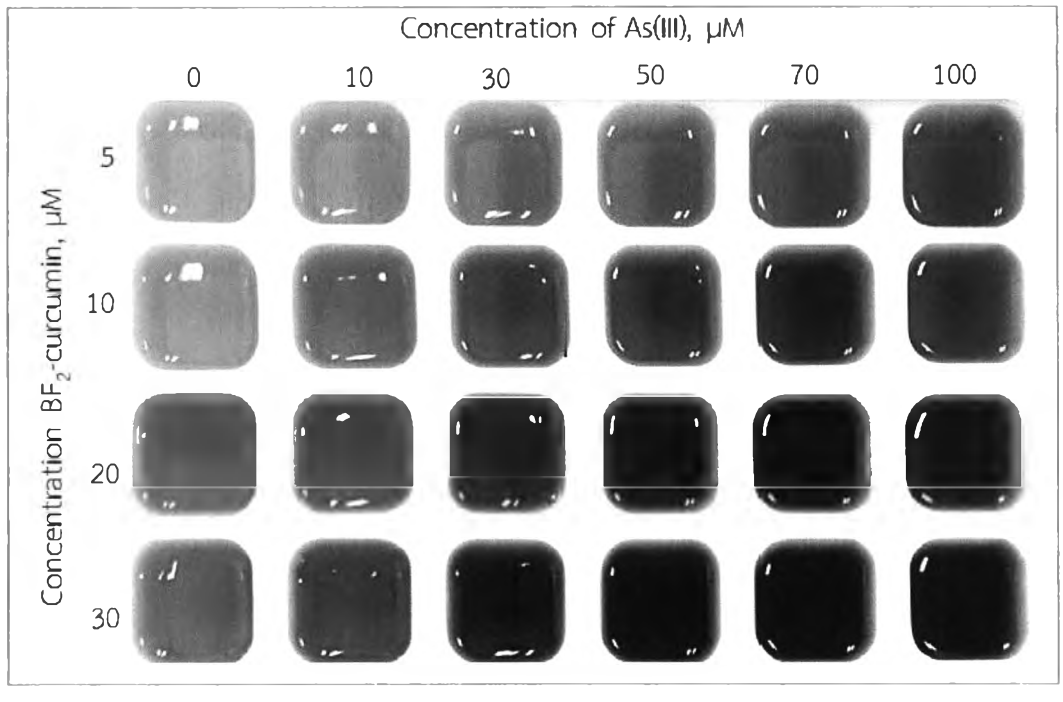


**Figure 4.4** The color of $BF_2$-curcumin solutions in various concentrations of As(III) solution from 0-100 μM.

### 4.2.2 Effect of pH

In this experiment, the pH of As(III) solution was varied by the addition of either 1M HCl and/or 1M NaOH solution. The photograph and the absorbance of $BF_2$-curcumin solutions with As(III) in various concentrations were shown in Figure 4.5 and Figure 4.6. At pH 3-7, the color of $BF_2$-curcumin solution with As(III) remained

orange suggesting that these environments are not favorable for the reaction. On the other hand, at pH 8-10 the color of solution turned to purple or blue and showed high absorbance at 632 nm. This observation could be explained by the species distribution of As(III) as shown in Figure 2.2(a). When the pH of As(III) solution was lower than 7, As(III) only exists as $H_3AsO_3$ but at pH 8, it began to dissociate and form oxyanion ($H_2AsO_3^-$), which can deprotonate the hydroxyl moiety of $BF_2$-curcumin molecule resulting in the change of solution color. The $BF_2$-curcumin solutions with deionized water at the same pH range were used as a control for comparative purpose. It was found that the color of these solutions were unchanged at pH 3-8 but turned to red at pH 9-10 and showed developing absorbances at 632 nm. To avoid any possible color or absorption interferences and false positive detection; therefore, pH 8 was chosen for further experiments.

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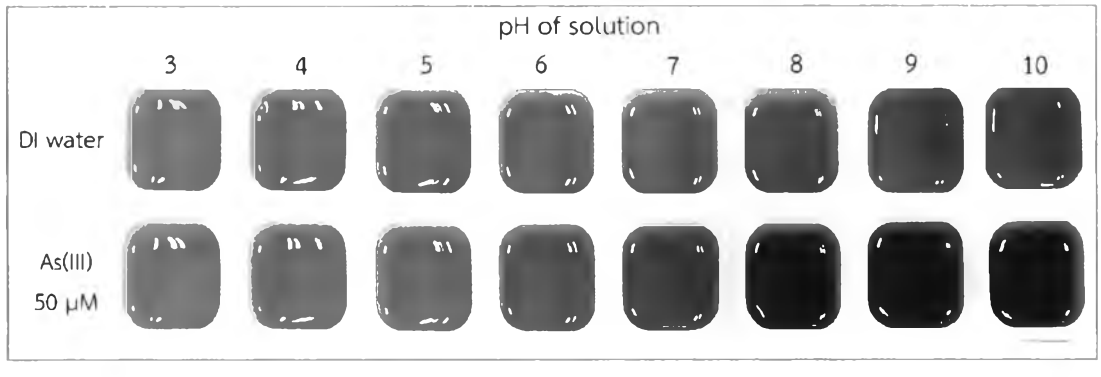


**Figure 4.5** The color of $BF_2$-curcumin in 50 μM As(III) solution and DI water at pH 3-10.

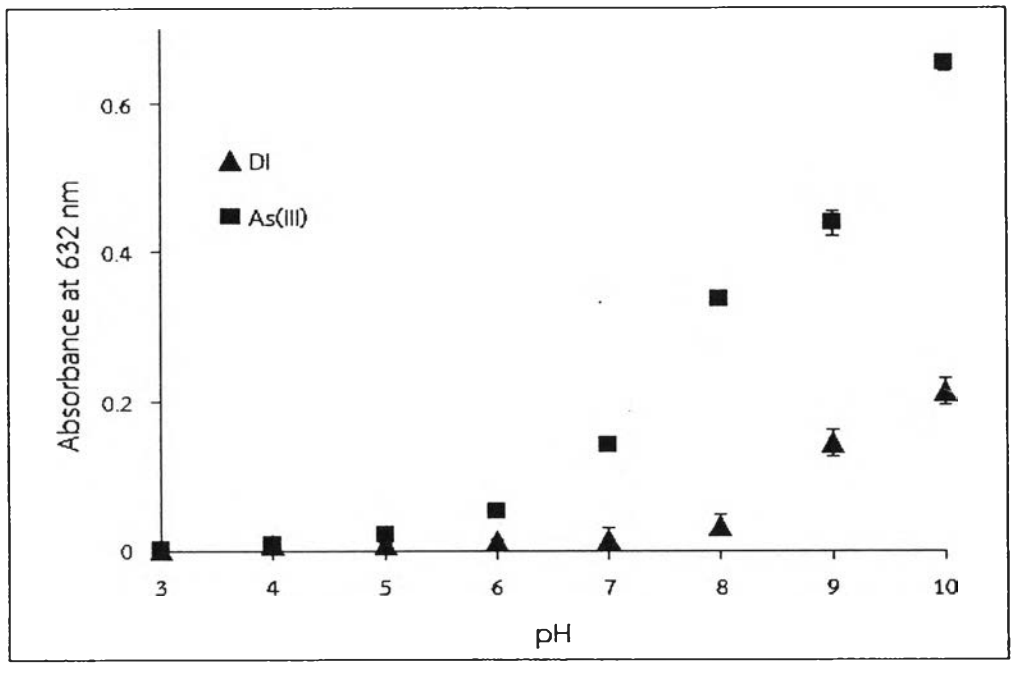


**Figure 4.6** The plot between absorbance at 632 nm of $BF_2$-curcumin in As(III) solution compared with DI water at pH 3-10.

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### 4.2.3 Sampling time

It was previously observed that following the addition of As(III) into the $BF_2$-curcumin solution, the color of solution rapidly turned to blue but faded away after time. Therefore, in this experiment, the sampling time was studied from 0-30 minutes. It was observed that the change of solution color and absorbance could be detected immediately after the addition of As(III) to $BF_2$-curcumin solution. Nonetheless, after approximately 3 minutes the solution color gradually blanched and the absorbance at 632 nm slightly decreased. The absorbance at 632 nm of $BF_2$-curcumin with 10, 50 and 80 μM As(III) at various sampling times were shown in Figure 4.7. It was clearly implied that the change of the solution color and its absorbance for the determination of As(III) by this method should be detected well within a reasonable time frame of roughly 3 minutes after adding As(III) to the $BF_2$-curcumin solution.

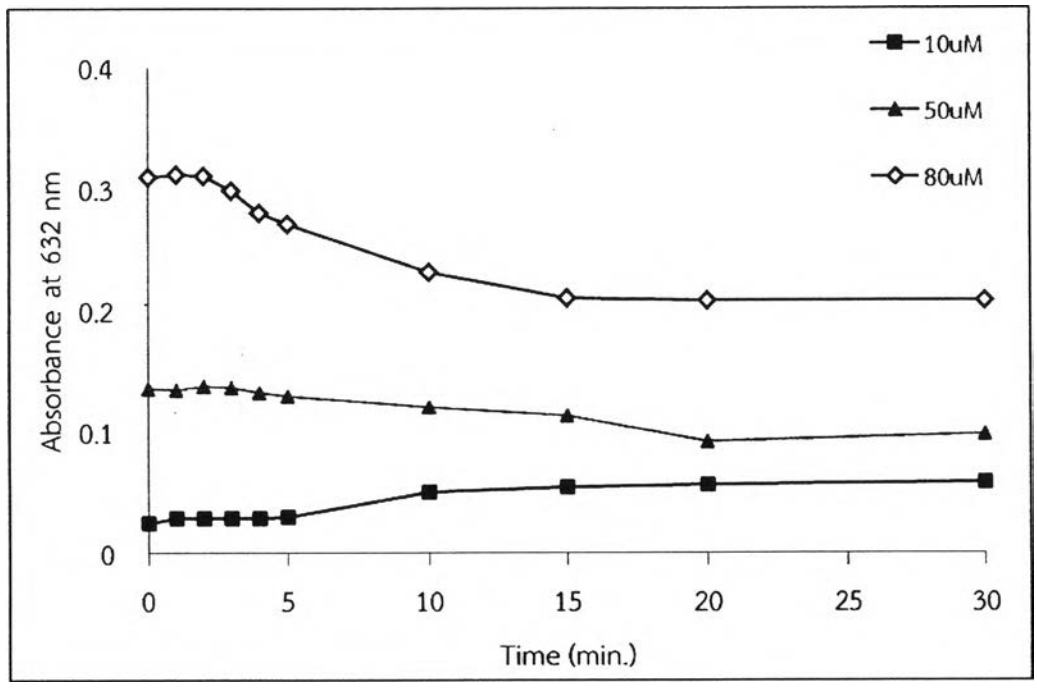


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**Figure 4.7** The absorbance at 632 nm of $BF_2$-curcumin with 10, 50 and 80 μM As(III) at various sampling times (0–30 min).

The fading of solution color was possibly due to the reaction between the deprotonated $BF_2$-curcumin and As(III) oxyanion remaining in the solution to form other complex. In addition, this phenomenon could also be effected by the fact that the deprotonated $BF_2$-curcumin could gain protons ($H^+$) from water molecules because the pH of the solution was not controlled with any buffer. This phenomenon can be confirmed by the slight increase of absorbance at 509 nm of $BF_2$-curcumin with 10, 50 and 80 μM As(III) at various sampling times (Figure 4.8).

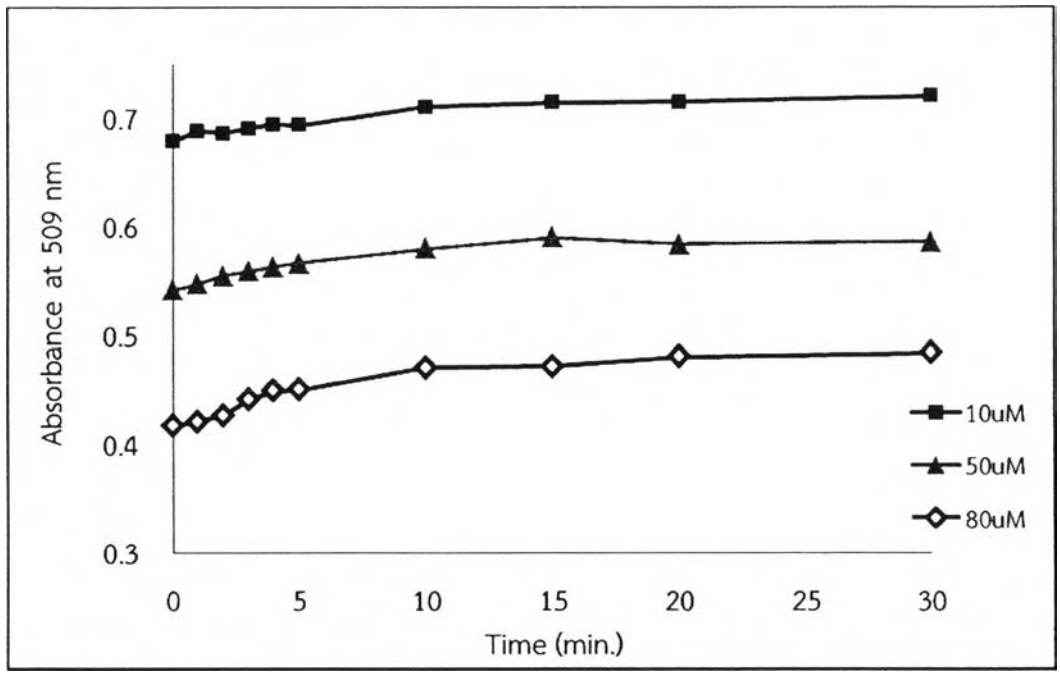


**Figure 4.8** The absorbance at 509 nm of $BF_2$-curcumin with 10, 50 and 80 μM As(III) at various sampling times (0–30 min).

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### 4.2.4 Interferences study

The colorimetric response of the $BF_2$-curcumin in the presence of various co-existing anions, i.e., $NO_3^-$, $I^-$, $CO_3^{2-}$, $S_2O_3^{2-}$, $PO_4^{3-}$ and $SO_4^{2-}$, at 1 mM each (10 folds) was studied and compared to the standard solution containing 100 μM of As(III). In Figure 4.9, the $BF_2$-curcumin solution did not exhibit the colorimetric response upon the addition of most anions, except for $CO_3^{2-}$ and $PO_4^{3-}$ with a strong response. As for the naked-eye detection, the color of $BF_2$-curcumin solution similarly turned from orange to blue in the presence of As(III), $CO_3^{2-}$ and $PO_4^{3-}$ as well. The photograph of $BF_2$-curcumin with As(III) and various anions is shown in Figure 4.10.

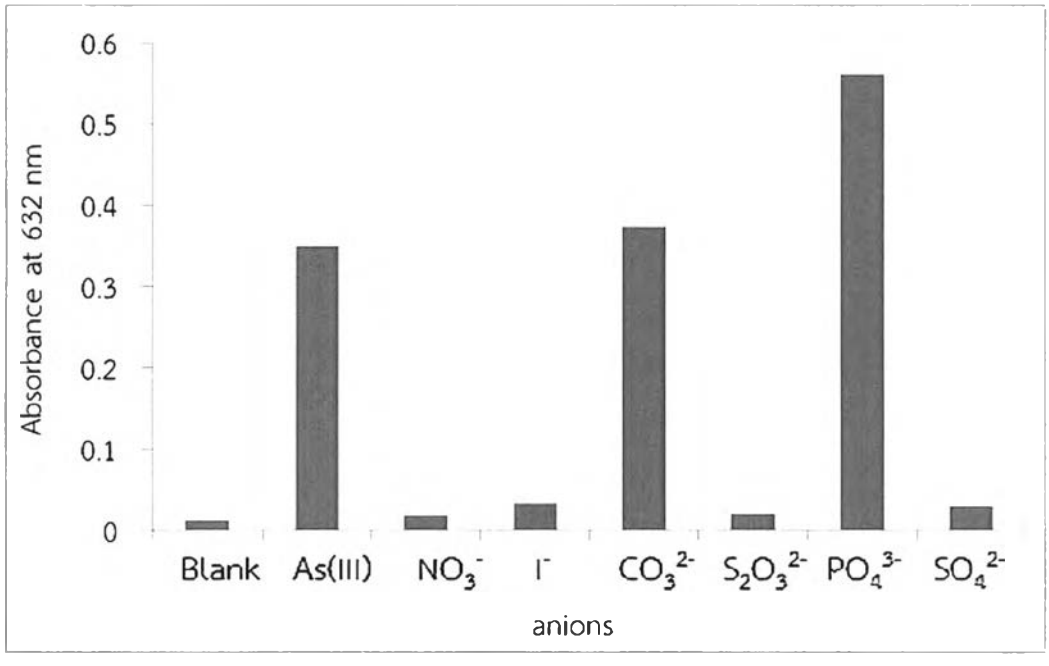


**Figure 4.9** Absorbance at 632 nm of $BF_2$-curcumin solution with 100 μM As(III) standard solution and $BF_2$-curcumin solution with 1mM of various anions.

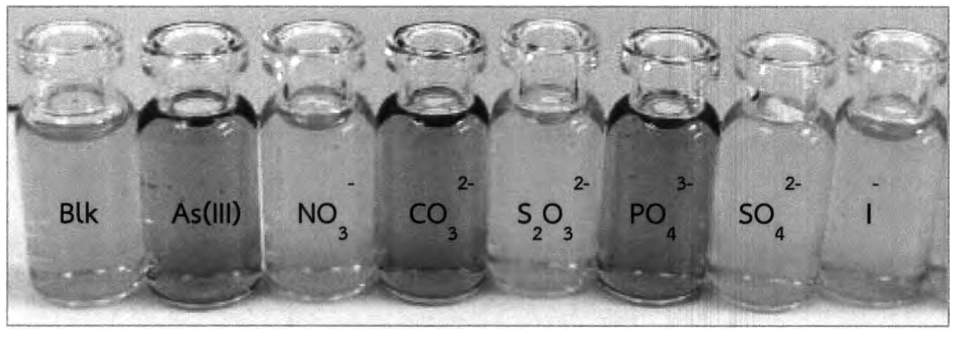


**Figure 4.10** The color of $BF_2$-curcumin with 100 μM As(III) and 1mM of various anions.

These observations suggested that the deprotonation of hydroxyl groups on $BF_2$-curcumin molecule was also affected by the presence of $CO_3^{2-}$ and $PO_4^{3-}$ which behave similarly to As(III) under this condition. $CO_3^{2-}$ and $PO_4^{3-}$ are conjugate base of weak acids ($H_2CO_3$ and $H_2PO_4^-$ which have low acid dissociation constant) and thus could likewise abstract protons from $BF_2$-curcumin at pH 8, which

was the optimal pH for this method. The removal of these ions are therefore deemed necessary prior to the colorimetric detection of As(III) using $BF_2$-curcumin. A variety of methods for eliminating $CO_3^{2-}$ and $PO_4^{3-}$ had been reported previously in the literatures, for example, the complete elimination of carbonate by converting to carbon dioxide gas after acidification [54] or the removal of phosphate using electrocoagulation [55] and the adsorption of phosphate by Al-based adsorbents [56].

### 4.2.5 Method validation

Under the optimal conditions, i.e. $BF_2$-curcumin concentration of 10 and 20 μM for naked eye detection and UV-Vis spectrometry, pH 8 of As(III) solution and sampling time within 3 minutes, the change in solution color of $BF_2$-curcumin was investigated by varying the concentration of As(III) from 0-500 μM. The photograph of the $BF_2$-curcumin solutions containing various concentration of As(III) solution from 0-500 μM was shown in Figure 4.11. This observation suggested that the changes of solution color from orange to blue are satisfactorily correlated with increasing concentrations of As(III). Nonetheless, the color of solution remained unchanged as blue at the concentration of As(III) above 100 μM. It was presumed that the complete deprotonation of the $BF_2$-curcumin molecules in the solution was established and no significant change was attained afterward.

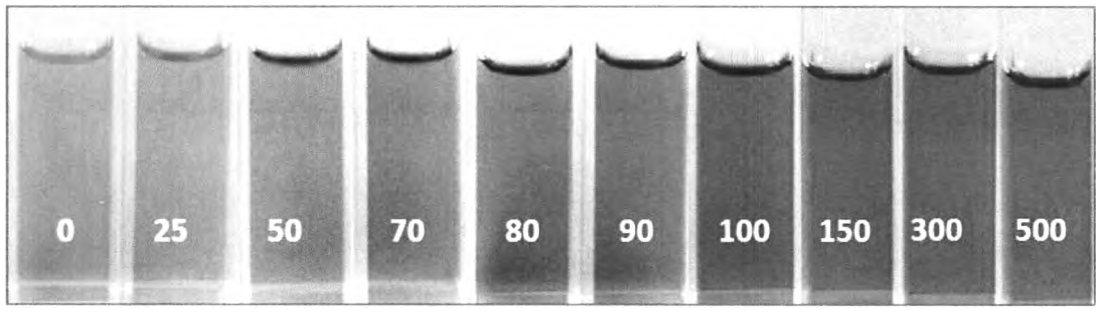


**Figure 4.11** The color of $BF_2$-curcumin solutions in various concentration of As(III) solution from 0-500 μM

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The lowest concentration of As(III) producing minimum change of color, was approximately 25 μM, corresponding to approximately 1:2 mole ratio of $BF_2$-curcumin/As(III). Although, the $BF_2$-curcumin (Figure 2.6) consists of two hydroxyl groups in its molecular structure and it can be deprotonated by two moles of As(III), the reaction may not be fully stoichiometric as it can be seen that the color of solution continually change with the increasing concentration of As(III) solutions. Based on this observation, the complete deprotonation of $BF_2$-curcumin was attained at roughly 100 μM As(III) which corresponded to approximately 1:10 mole ratio of $BF_2$-curcumin/As(III). Therefore, this concentration range could be usefully employed for the determination of As(III).

The color changes of $BF_2$-curcumin solution with As(III) standard solutions in the concentration 0, 25, 50, 70, 90 and 100 μM were used as a color calibration chart for naked eye detection of As(III). This color calibration chart for naked eye detection of As(III) in solution system is shown in Figure 4.12. The LOD, estimated by the lowest concentration of As(III) that produce the minimum change of color which can be visually differentiated from that of the blank solution, was found to be 25 μM (1.87 mg/L). The LOD of this work in terms of naked eye detection was compared with the previous work (modified gold nanoparticles) [37]. Although the LOD of this method is relatively higher than the previous work, it does offer some unique advantages like being very simple, rapid and low cost method for As(III) determination.

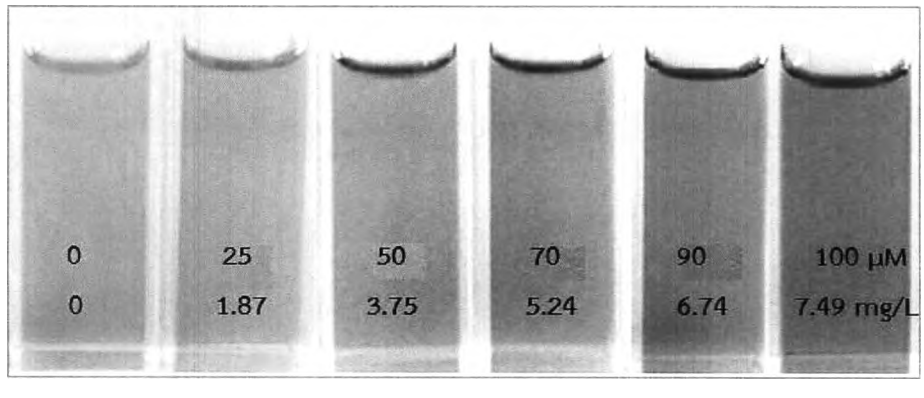


**Figure 4.12** The color calibration chart for naked eye detection of As(III) in solution system.

In terms of UV-Vis spectrophotometry, the absorption spectra of $BF_2$-curcumin with varying concentrations of As(III) from 0 to 100 μM were obtained as shown in Figure 4.13. The maximum absorbance of $BF_2$-curcumin at 509 nm decreased while the absorbance at 632 nm continually increased as the concentration of As(III) increased. The calibration curve was plotted by using the concentration of As(III) in the range of 2-100 μM in Figure. 4.14. The linear response was clearly observed in two different concentration levels: the lower concentration level of 2-30 μM with the linear equation of y=0.0065x-0.0002 and $R^2$=0.9954, and the higher concentration level of 30-100 μM with the linear equation of y=0.0115x-0.1638 and $R^2$=0.9972, respectively. The limit of detection (LOD), based on 3 times of standard deviation of blank signal, was estimated to be 0.26 μM (19.8 μg/L) with the relative standard deviation (RSD) of 2.01% (n=10). The LOD of this work in terms of UV-Vis spectrophotometry was lower than the previous method (Rhodamine-B) [36].

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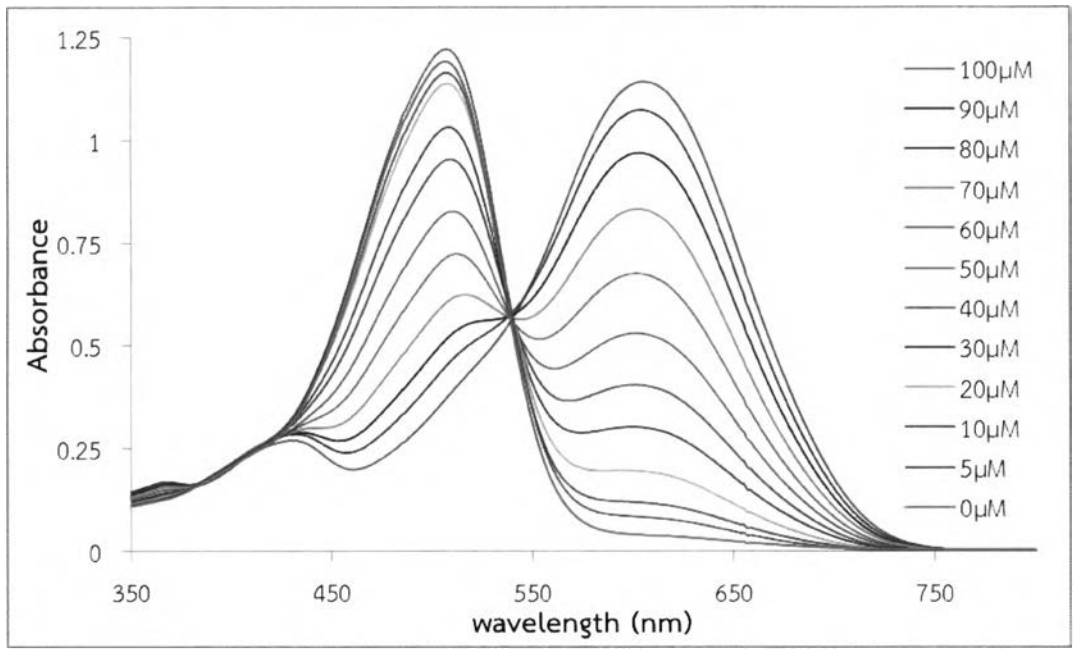


**Figure 4.13** The UV-visible spectra of $BF_2$-curcumin solution with varying concentrations of As(III) 0-100 μM

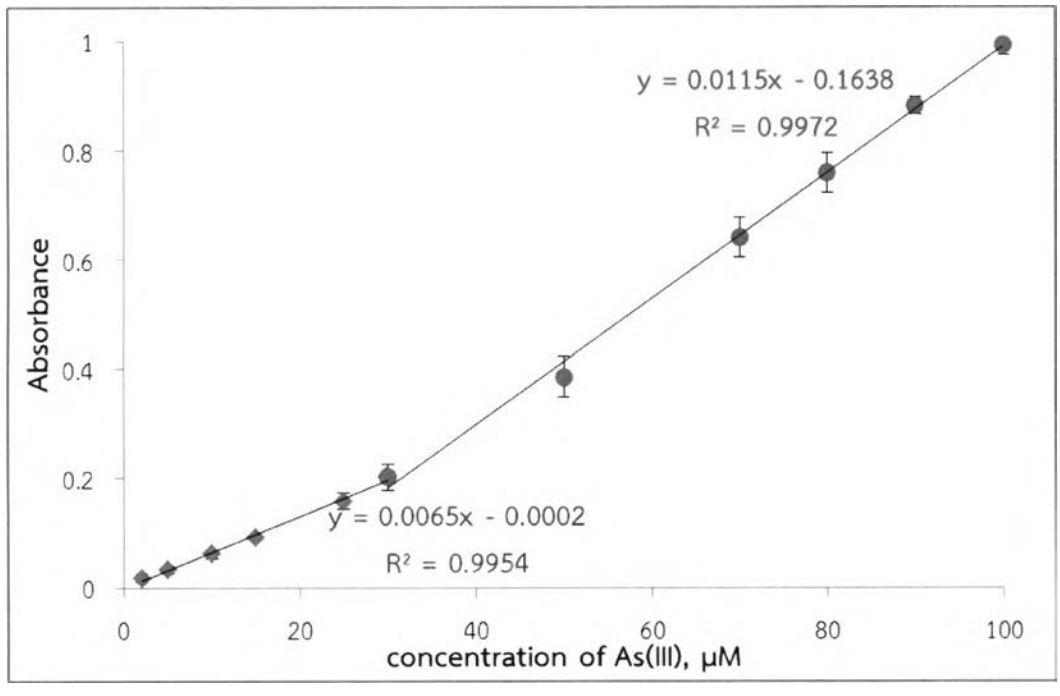


**Figure 4.14** The calibration curve of $BF_2$-curcumin solution with As(III) 2-100 µM obtained under optimal condition.

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Based on previous results, the $BF_2$-curcumin colorimetric method was clearly favorable for the determination of As(III) over As(V). Thus, the determination of total As would require an additional step to reduce As(V) to As(III). In this experiment, the As(V) was reduced with 5% KI-ascorbic acid [57] before the determination and the efficiency of the reduction of As(V) to As(III) are shown in Table 4.1. The efficiency of the reduction is shown as %reduction which calculated from Equation 4.1.

$$\%\text{reduction} = \frac{Ca}{Cb} \times 100 \qquad (4.1)$$

when Ca = the concentration of As(III) found in the sample by this method after reduction (µM)

Cb = the concentration of As(V) added in the sample (µM)

**Table 4.1** Concentration of As(III) after reduction with 5% KI-ascorbic acid found by this method

| Added concentration of As(V), μM | Found concentration of As(III) after reduction, μM | %reduction |
|---|---|---|
| 10.00 | 11.90 | 119.0±7.6 |
| 20.00 | 15.42 | 77.09±2.1 |
| 40.00 | 19.56 | 48.89±1.9 |
| 60.00 | 29.17 | 48.62±0.5 |

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The results showed that the reduction efficiency of As(V) with 5% KI-ascorbic acid were rather low in higher As(V) concentration. Therefore, the reduction of As(V) to As(III) by 5% KI-ascorbic acid was not suitable for the determination of total As by $BF_2$-curcumin.

However, it was interestingly found that under the optimal condition, As(V) produced nearly identical response and recovery as that of As(III) within a certain concentration range. The absorption spectra of $BF_2$-curcumin with the addition of As(III) compared with those of As(V) in the concentration range of 0-70 μM were shown in Figure 4.15. Based on this observation and further experimental trials, it was concluded that this method can be readily used for the determination of As(III) and As(V) as accurately as total arsenic of both species within the concentration range of roughly 0-60 μM without the necessity of any reduction step.

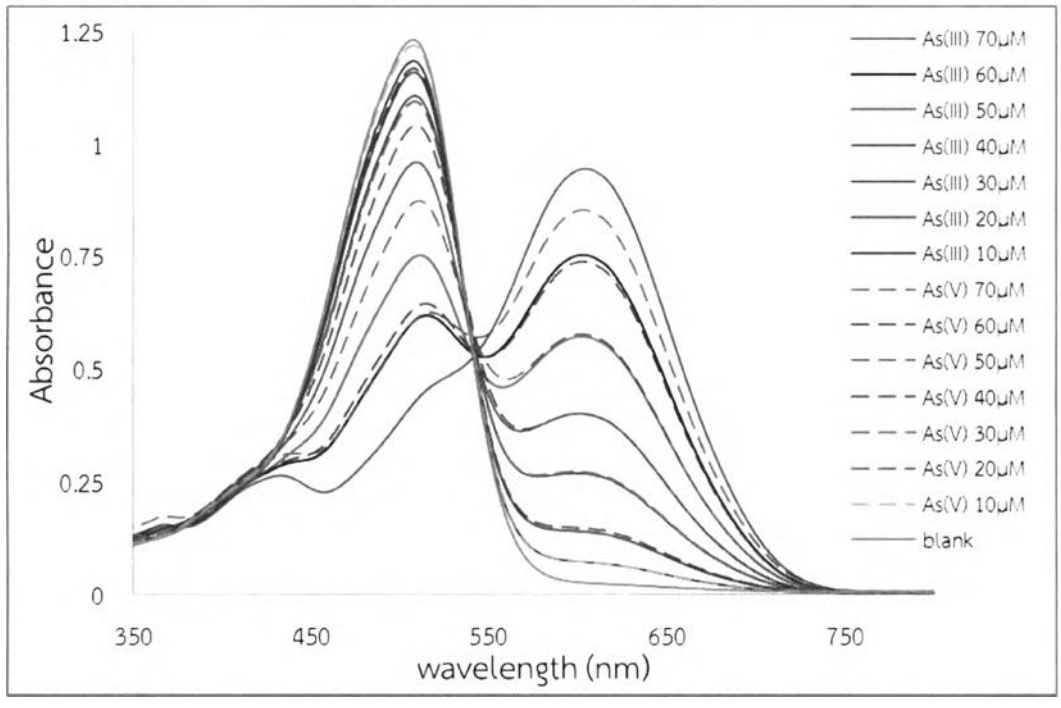


**Figure 4.15** The absorption spectra of $BF_2$-curcumin with the addition of As(III) compared with As(V) in the concentration range 0-70 μM

## 4.3 Naked eye detection of arsenic in solid system

### 4.3.1 Characterization of $BF_2$-curcumin coated resin

The coating of this resin with $BF_2$-curcumin can significantly impact the naked eye detection of As(III). Thus, the characterization of resin was necessary to verify the coating of the material. The $BF_2$-curcumin coated resin was characterized by Fourier transform infrared spectroscopy (FT-IR), Fourier transform Raman spectroscopy (FT-Raman) and diffuse reflectance ultraviolet visible spectrophotometry (DR-UV-Vis).

#### Fourier Transform Infrared Spectroscopy (FT-IR)

The IR spectra of the reins were recorded by using ATR mode. The IR spectrum of Amberlite XAD-2 resin presented three characteristic peaks, $\nu$(=C-H) at 3018 $cm^{-1}$, $\nu$(Ar C=C) at 1599 and 1402 $cm^{-1}$, and $\nu$(C-H) at 2923 $cm^{-1}$ [47, 58] (Figure

4.16(a)). The IR spectrum of $BF_2$-curcumin (Figure 4.16(h)) showed characteristic peaks, ν(Ar C=C) at 1608 and 1391 $cm^{-1}$ and ν(O-H) at 3484 $cm^{-1}$. After coating of the resin with $BF_2$-curcumin in various concentrations of 5, 10, 20, 30, 50 and 70 μM, these resins showed peaks at 3018, 2923 1597 and 1402 $cm^{-1}$, which were similar to those of Amberlite XAD-2 resin (Figure 4.16(b)-(g)). However, the characteristic peaks of $BF_2$-curcumin did not appear in the spectrum of $BF_2$-curcumin coated resins, presumably due to the presence of only trace amount of $BF_2$-curcumin on the resin surface. Therefore, the coating of $BF_2$-curcumin onto resins cannot be confirmed by FT-IR.

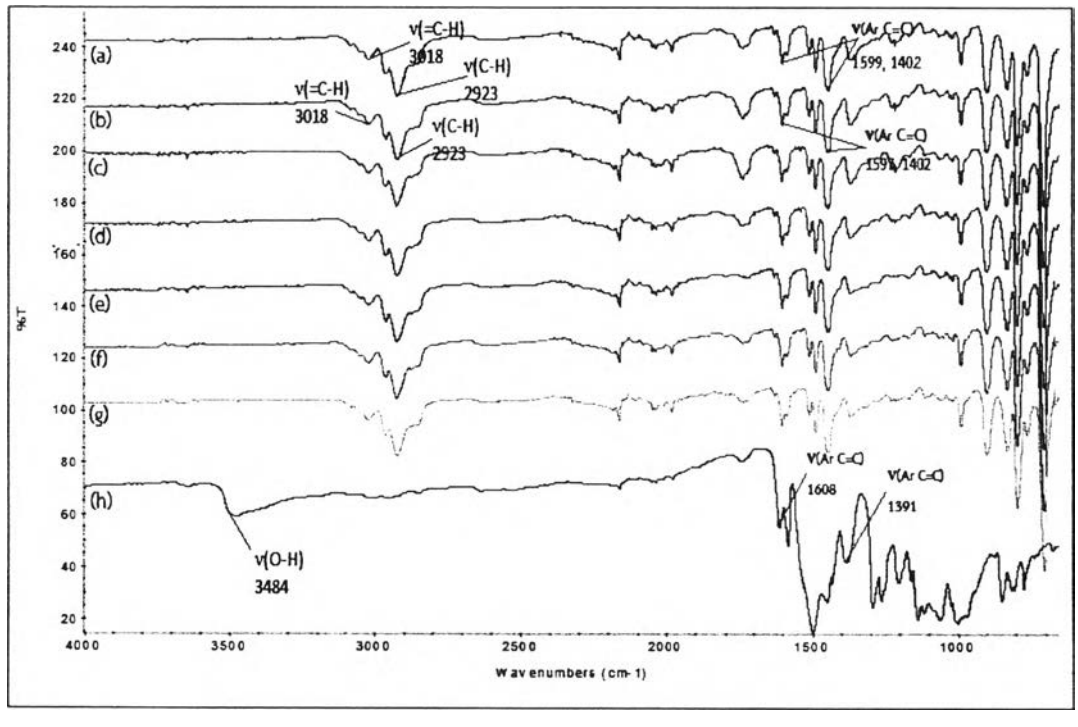


**Figure 4.16** IR spectra of (a) Amberlite XAD-2 resin, (b)-(g) $BF_2$-curcumin coated resin with various concentrations of 5, 10, 20, 30, 50 and 70 μM and (h) $BF_2$-curcumin.

### Fourier Transform Raman Spectroscopy (FT-Raman)

The Raman spectrum of Amberlite XAD-2 resin showed three characteristic peaks, ν(C=H) at 3062 $cm^{-1}$, ν(Ar C=C) at 1605 $cm^{-1}$, and aromatic monosubstituted at 998 $cm^{-1}$ [58] (Figure 4.17(a)). After coating the resin with $BF_2$-curcumin in various concentrations of 10, 30, 50 and 70 μM, these coated resins showed similar Raman spectrum as that of amberlite XAD-2 resin. The Raman spectra of $BF_2$-curcumin coated resin with various concentrations of 10, 30, 50 and 70 μM were shown in Figure 4.17(b)-(e). It was found that the peaks of $BF_2$-curcumin did not appear in the Raman spectrum of $BF_2$-curcumin coated resin probably because there are very trace amount of $BF_2$-curcumin on the resin surface. Thus, the coating of $BF_2$-curcumin onto resins cannot be confirmed by FT-Raman.

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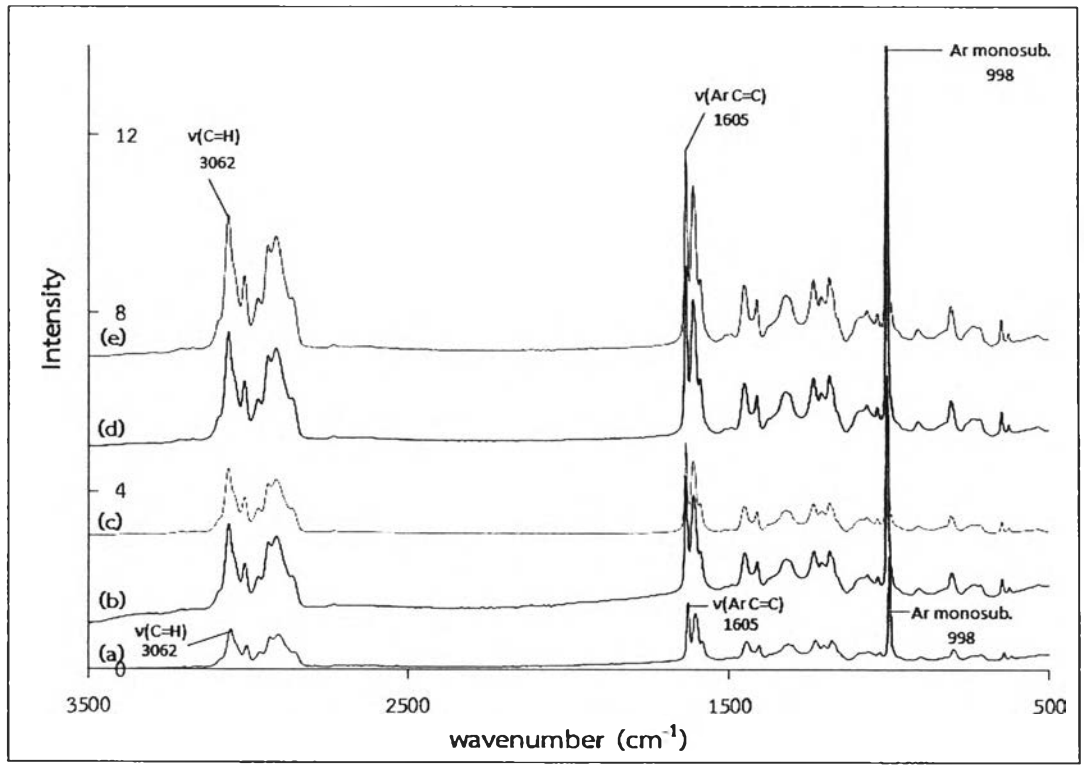


**Figure 4.17** Raman spectra of (a) Amberlite XAD-2 resin, (b)-(e) $BF_2$-curcumin coated resin with various concentrations of 10, 30, 50 and 70 μM.

**Diffuse reflectance ultraviolet visible spectrophotometry**

Another technique utilized to confirm and identify the coating of resin was a DR-UV-Vis spectrophotometry. The result showed that the maximum absorbance of $BF_2$-curcumin on Amberlite XAD-2 resin at 498 nm constantly increased with the concentration of $BF_2$-curcumin. The DR-UV-Vis spectra of $BF_2$-curcumin coated resin with various concentration of $BF_2$-curcumin for the preparation of the coated resin were shown in Figure 4.18.

In conclusion, DR-UV-Vis spectrophotometric result was able to confirm the success of the coating of $BF_2$-curcumin onto resin.

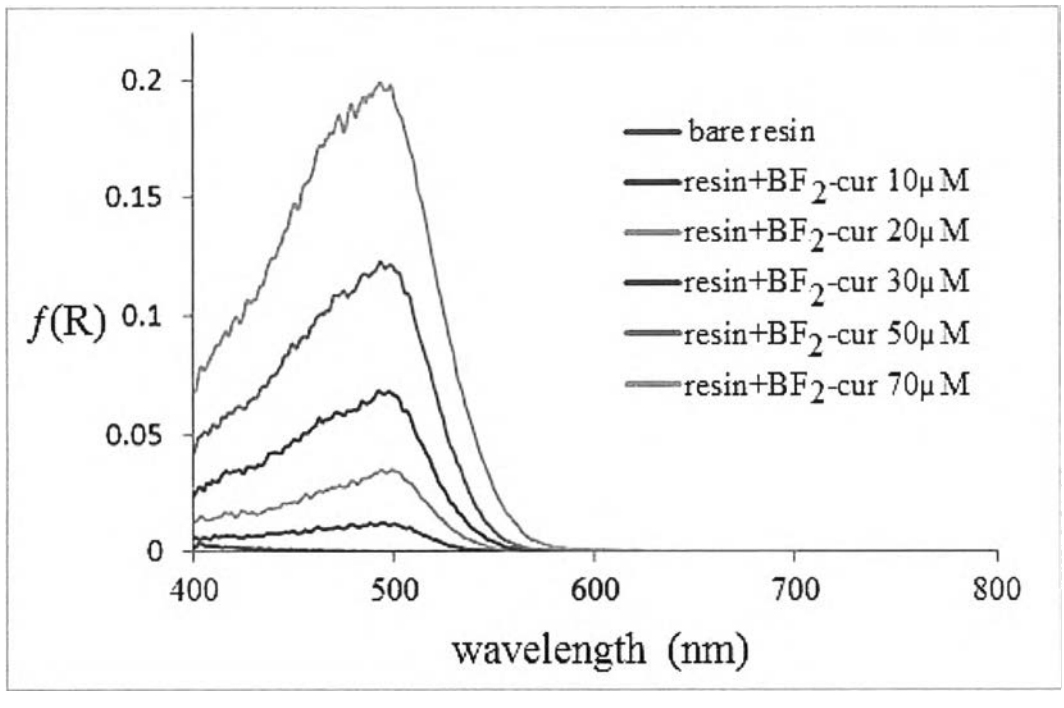


**Figure 4.18** DR-UV-Vis spectra of $BF_2$-curcumin-coated resin with various concentration of $BF_2$-curcumin for the preparation of the coated resin.

Amberlite XAD-2 resin is a hydrophobic cross-linked polystyrene copolymer and it has nonionic structure that can adsorb nonpolar substances on its surface [46]. The $BF_2$-curcumin is classified as a nonpolar substance that has low aqueous solubility. From this coating step, it was found that $BF_2$-curcumin can be

immobilized onto the Amberlite XAD-2 resin surface. Therefore, the $BF_2$-curcumin was believed to have interacted and attached with Amberlite XAD-2 resin via van der Waals force between nonpolar-nonpolar substances [59-61].

### 4.3.2 Effect of pH

The pH of As(III) solution was investigated in the range of pH 3-10. The resulting color of coated resin in As(III) solution was still orange at pH 3-9, while the color of the resin turned to blue at pH 10 which can be clearly observed by naked-eyes. The color of $BF_2$-curcumin (70 μM) coated resin in As(III) solution pH 3-10 were shown in Figure 4.19. Comparing this result with coated resin in the blank solution (deionized water) in the same pH range, it was found that the color of these coated resins did not change. Therefore, the pH 10 of As(III) solution was chosen for further experiments.

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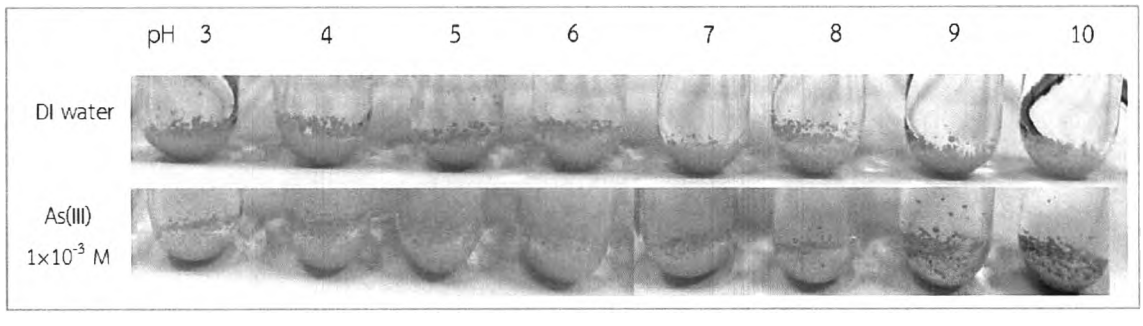


**Figure 4.19** The color of $BF_2$-curcumin coated resin in As(III) solution and DI water at pH range 3-10.

It was noted that the optimal pH in the solid system (pH 10) was higher than the optimal pH in the solution system (pH 8), this can be described by two possible aspects as followed. First, unlike the solution, the $BF_2$-curcumin molecules in the solid system were not freely dispersed because they were attached on the resin surface. Hence, the possibility of the reaction between $H_2AsO_3^-$ in the solution and the $BF_2$-curcumin molecules on the resin surface was less favorable than that in the solution system. According to the distribution of As(III) species in

Figure 2.2(a), the amount of $H_2AsO_3^-$ increased over the pH ranging from 8 to 10. Therefore, higher pH was required in the solid system to increase the amount of the $H_2AsO_3^-$ which could then lead to the enhanced possibility of the deprotonation. The second aspect is that the $BF_2$-curcumin in the solid system interacted and attached with Amberlite XAD-2 resin via van der Waals force and the proton of the hydroxyl moiety of $BF_2$-curcumin molecule also interacted with Amberlite XAD-2 resin via van der Waals force, thus the deprotonation was less favorable. However at pH 10 (Figure 2.2(a)), As(III) exists as $H_2AsO_3^-$ and even $HAsO_3^{2-}$, which is a stronger base that can abstract the proton from the $BF_2$-curcumin on the resin surface. Thus, the $BF_2$-curcumin on resin surface can be deprotonated by As(III) solution at pH 10.

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### 4.3.3 Effect of concentration of $BF_2$-curcumin for coating resin

The concentration of $BF_2$-curcumin solution was varied in the range of 10-70 μM in preparation of the coated resin. When the concentration of $BF_2$-curcumin increased, the color of resin changed from light orange to dark orange which could inevitably obscure the color for the naked-eye detection of As(III) on the coated resin. (Figure 4.20 and Table 4.2) However, it was found that the $BF_2$-curcumin solution in the concentration of 50 μM exhibited a clear and distinct change of the resin color from orange to blue by the increase of As(III) concentration. Therefore, this concentration was chosen as optimal for the preparation of $BF_2$-curcumin coated resin for the following experiments.

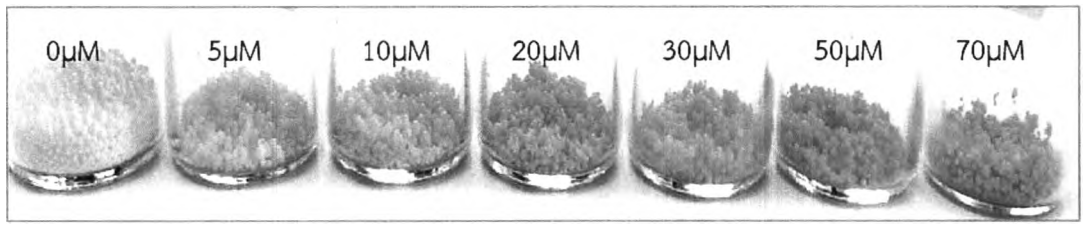
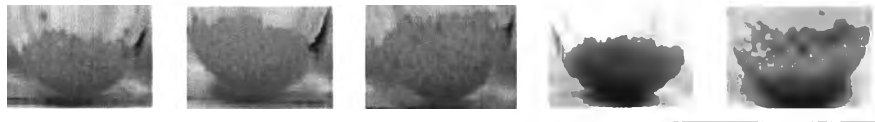



**Figure 4.20** The color of coated resin with various concentration of $BF_2$-curcumin solution.

**Table 4.2** Effect of concentration of $BF_2$-curcumin solution for As(III) determination at pH 10

| Concentration of $BF_2$-curcumin, μM | Concentration of As(III), M | | | | |
|---|---|---|---|---|---|
| | 0 | $1\times10^{-6}$ | $1\times10^{-5}$ | $1\times10^{-4}$ | $1\times10^{-3}$ |
| 10 |  | | | | |
| 20 |  | | | | |
| 30 |  | | | | |
| 50 |  | | | | |
| 70 |  | | | | |

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### 4.3.4 Method validation

From the preliminary study of the naked eye detection of arsenic by $BF_2$-curcumin solution, the color of the $BF_2$-curcumin solution with As(V) turned to blue but it was observed that the solution color was less differentiated when compared with the solution color of $BF_2$-curcumin with As(III). Thus, in term of naked eye detection, As(III) was selected for the performance evaluation of the method using $BF_2$-curcumin solution and also the method using $BF_2$-curcumin coated resin.

Under the optimal conditions, i.e. 50 μM of $BF_2$-curcumin coated resin and pH 10 of As(III) solution, the color of the resin changed progressively from orange to blue in correlation with the concentrations of standard As(III) solution from 0 to $5\times10^{-3}$ M. The photograph of the color of $BF_2$-curcumin-coated resin in the standard

solutions containing different concentrations of As(III) was shown in Figure 4.21. These resin color were used as a color calibration chart for naked eye detection of As(III).

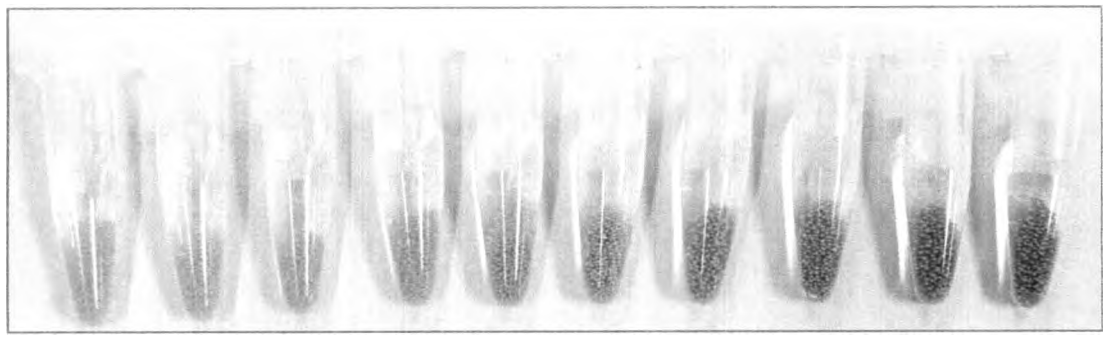

**Figure 4.21** The colors of $BF_2$-curcumin-coated resin in the standard solutions containing different concentrations of As(III) from 0, $1\times10^{-7}$, $1\times10^{-6}$, $1\times10^{-5}$, $3\times10^{-5}$, $5\times10^{-5}$, $1\times10^{-4}$, $5\times10^{-4}$, $1\times10^{-3}$ and $5\times10^{-3}$ M, from left to right.

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After being evaluated by ICP-OES, it was found that the residual As(III) concentration were similar to the initial As(III) concentration in all solutions. Thus, the proposed reaction mechanism that the As(III) oxyanions did not take part directly into forming a complex with ligand but only abstract protons from the hydroxyl moiety of $BF_2$-curcumin molecule on the coated resin was confirmed. In this procedure, the LOD of As(III) was $3\times10^{-5}$ M or 2.25 mg/L by the observation of the change of the resin color that can be differentiated with naked-eyes.

For total As determination, a mixture of As(III) and As(V) (1:1) was used as a sample to investigate the application of this method in the same manner. The color of $BF_2$-curcumin coated resin change accordingly with the total As concentration but the range of color was different when compared with As(III) solution. The changes of resin color in total As standard solutions in the concentration 0, $3\times10^{-5}$, $1\times10^{-4}$, $5\times10^{-4}$, $1\times10^{-3}$ $2\times10^{-3}$ and $5\times10^{-3}$ M were used as the color calibration chart for naked eye detection of total As in water samples. The photograph of the color calibration chart for naked eye detection of total As in solid

system was shown in Figure 4.22. The LOD of this method for total As was $1\times10^{-4}$ M or 7.5 mg/L.

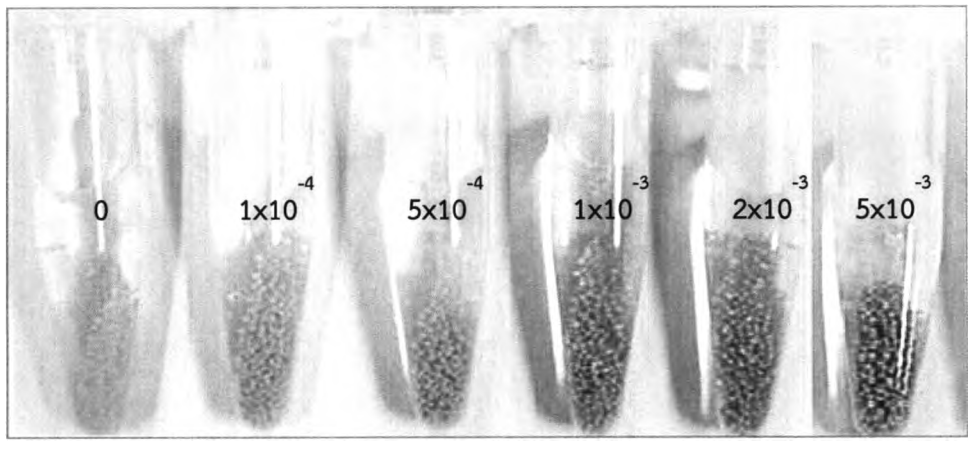


**Figure 4.22** The color calibration chart for naked eye detection of total As in solid system.

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### 4.3.5 Regeneration of $BF_2$-curcumin coated resin

The used resin can be regenerated by the protonation of the $BF_2$-curcumin with 1 M HCl solution as indicated by the color of the resin that is rapidly turning from blue to orange. After that, the resin was washed with deionized water before the next use. The regenerated resin can be used again for the determination of As(III) with a normal color changing from orange to blue. This suggested that the used resin can be regenerated and repeatedly used for naked-eye detection of As(III).

## 4.4 Application in real samples

### 4.4.1 Determination of As(III) in water samples

#### 4.4.1.1 Solution system

In terms of UV-Vis spectrophotometry, a commercial bottled drinking water was sampled for the determination of As(III) using this method. Because no As(III) was essentially contaminated in this sample, the recovery of the

spiked sample was employed to validate the accuracy of this method instead. The changes in color of the solutions were observed together with the absorbance monitored by a UV-visible spectrophotometer at 632 nm. The recoveries of the spiked real water samples containing 10, 25, 50 and 75 μM of As(III) were shown in Table 4.3.

**Table 4.3** Concentration of As(III) in spiked bottled water sample found by this method

| Added concentration of As(III), μM | Found concentration of As(III), μM | %recovery |
|---|---|---|
| 0.00 | nd | - |
| 10.00 | 10.94 | 109.4±0.1 |
| 25.00 | 25.46 | 101.8±0.5 |
| 50.00 | 46.78 | 93.66±1.3 |
| 75.00 | 67.05 | 89.40±2.1 |

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The results showed that the accuracy and precision of this proposed method for As(III) detection were acceptable, according to the criteria of analyte recovery in different concentration levels [62], as shown in Table 4.4.

Table 4.4 Analyte recovery and precision at different concentration [62]

| Analyte (%) | Analyte Ratio | Unit | Mean Recovery (%) | RSD (%) |
|---|---|---|---|---|
| 100 | 1 | 100% | 98-102 | 1.3 |
| 10 | $10^{-1}$ | 10% | 98-102 | 2.8 |
| 1 | $10^{-2}$ | 1% | 97-103 | 2.7 |
| 0.1 | $10^{-3}$ | 0.1% | 95-105 | 3.7 |
| 0.01 | $10^{-4}$ | 100 ppm | 90-107 | 5.3 |
| 0.001 | $10^{-5}$ | 10 ppm | 80-110 | 7.3 |
| 0.0001 | $10^{-6}$ | 1 ppm | 80-110 | 11 |
| 0.00001 | $10^{-7}$ | 100 ppb | 80-110 | 15 |
| 0.000001 | $10^{-8}$ | 10 ppb | 60-115 | 21 |
| 0.0000001 | $10^{-9}$ | 1 ppb | 40-120 | 30 |

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In terms of naked eye detection, a bottled drinking water and Chulalongkorn University's pond water were used as samples to study the application of this method. The color of $BF_2$-curcumin solution did not change with water sample because the concentration of As(III) in water sample was lower than the LOD of the naked eye detection (25 μM or 1.87 mg/L). Thus, the sample with spiked As(III) in the concentration of 30, 50, 70 and 130 μM, were employed to validate the accuracy of this method by comparing with the color calibration chart of the As(III) standard solutions in Figure 4.12. The color of $BF_2$-curcumin solution with the spiked real water samples were shown in Figure 4.23.

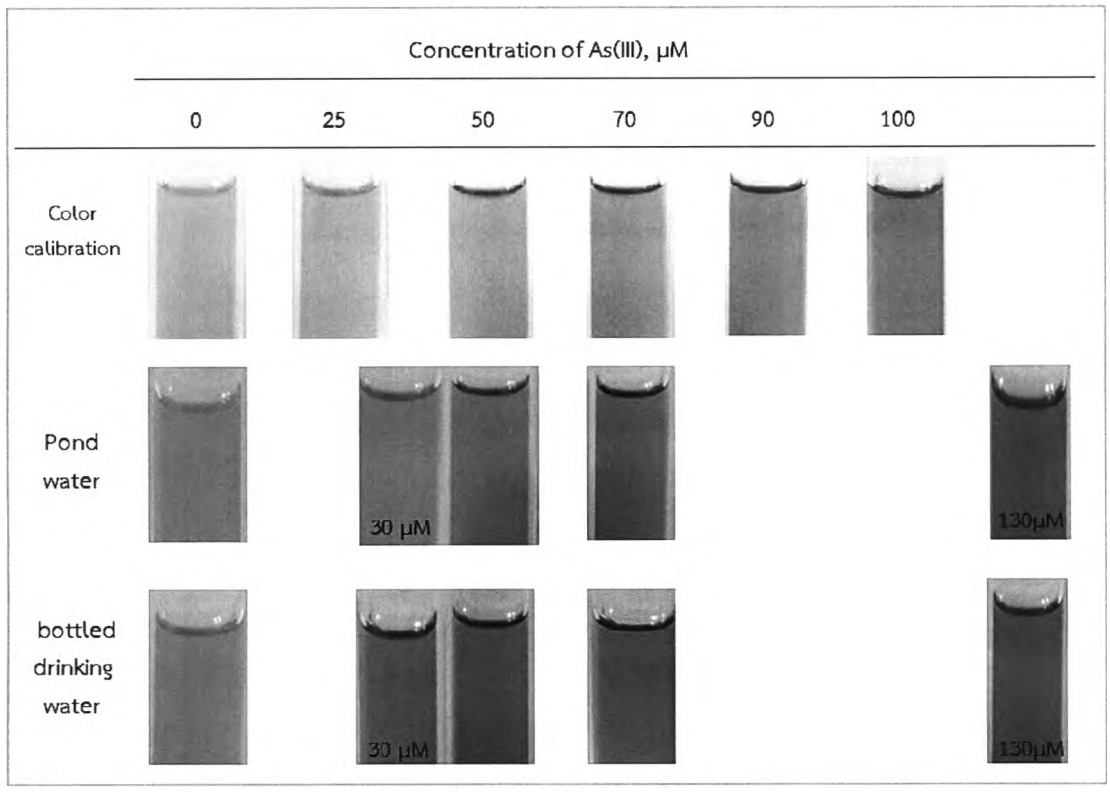


**Figure 4.23** The color of $BF_2$-curcumin solution applied with the spiked pond water and drinking water.

These results demonstrated that the accuracy of naked-eye As determination in spiked samples were acceptable and the color of $BF_2$-curcumin with spiked water samples were similar when compared with the color calibration chart of As(III) standard solution of equivalent concentration. Therefore, this result suggested that this procedure can be applied for the determination of As(III) in water sample by UV-Visible spectrometry and naked eye detection in solution system.

#### 4.4.1.2 Solid system

In the solid system, this proposed method was applied to detect As(III) in Chulalongkorn University's pond water. The color of the $BF_2$-curcumin-coated resin did not change when it was initially attempted to analyze the pond water sample. It was presumed that the As(III) concentration was lower than the LOD

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of this method. Therefore, the procedures were re-applied to the pond water samples spiked with As(III) in the concentration of $3\times10^{-5}$, $5\times10^{-4}$ and $1\times10^{-3}$ M, respectively. The photographs of $BF_2$-curcumin-coated resin applied with the spiked samples are shown in Figure 4.24.

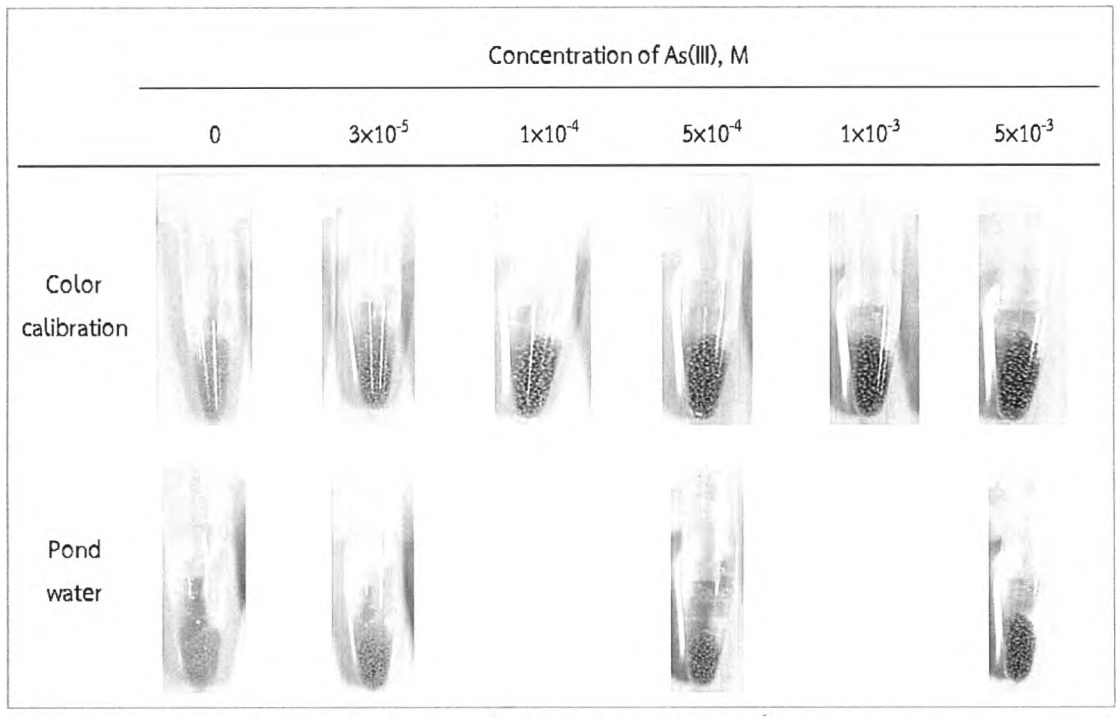


**Figure 4.24** The color of $BF_2$-curcumin-coated resin applied with the spiked pond water.

The results demonstrated that the color of the coated resins obtained in this application were similar and in good agreement with those of the color calibration chart of As(III) standard solutions (Figure 4.21). These results implied that the proposed method can be applied for the screening test of As(III) in natural surface water samples by naked-eye detection.

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### 4.4.2 Determination of total As in water samples

#### 4.4.2.1 Solution system

A bottled drinking water was used as a sample to study the application of this method for determination of total As (As(III) and As(V) in 1:1 ratio). Because no As(III) was contaminated in this sample, the recovery of the spiked sample was employed to validate the accuracy of this method. This method was applied with spiked drinking water samples with As(III) in the concentration range of 10, 30 and 50 μM. For the changes in color of the solutions visually observed were unclear, the changes in absorbance of the solution were used instead. The recoveries of the spiked drinking water samples containing 10, 30, 50 μM of As(III) were shown in Table 4.5. The results showed that the accuracy and precision of this proposed method for total As detection were acceptable, according to the criteria of analyte recovery in different concentration levels [62], (Table 4.4).

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**Table 4.5** Concentration of total As in spiked bottled water sample by this method

| Added concentration of As(III), μM | Found concentration of As(III), μM | %recovery |
|---|---|---|
| 0.00 | nd | - |
| 10.00 | 9.00 | 90.0±1.1 |
| 30.00 | 32.45 | 108.16±1.5 |
| 50.00 | 54.05 | 108.10±1.8 |

#### 4.4.2.2 Solid system

In terms of solid system, 2 types of waste water samples (TK80 and TK81) from the PTT Public Company Limited were used as samples. The resin color in samples rapidly changed from orange to pale blue when the test was performed. Then the concentration of total As in samples were evaluated by comparing with a

color calibration chart of total As standard solution in Figure 4.22. It was found that the concentration of total As in waste water samples TK80 and TK81 were approximately $1\times10^{-3}$-$2\times10^{-3}$ M or 75-150 mg/L. The photograph of the color of $BF_2$-curcumin-coated resin applied with the waste water samples was shown in Figure 4.25. These results were compared with those obtained from ICP-OES measurement of the same samples as summarized in Table 4.6. The present naked eye detection on $BF_2$-curcumin coated resin produced good agreement with the result of ICP-OES. Therefore, the proposed procedure can be used for the screening of As in waste water samples.

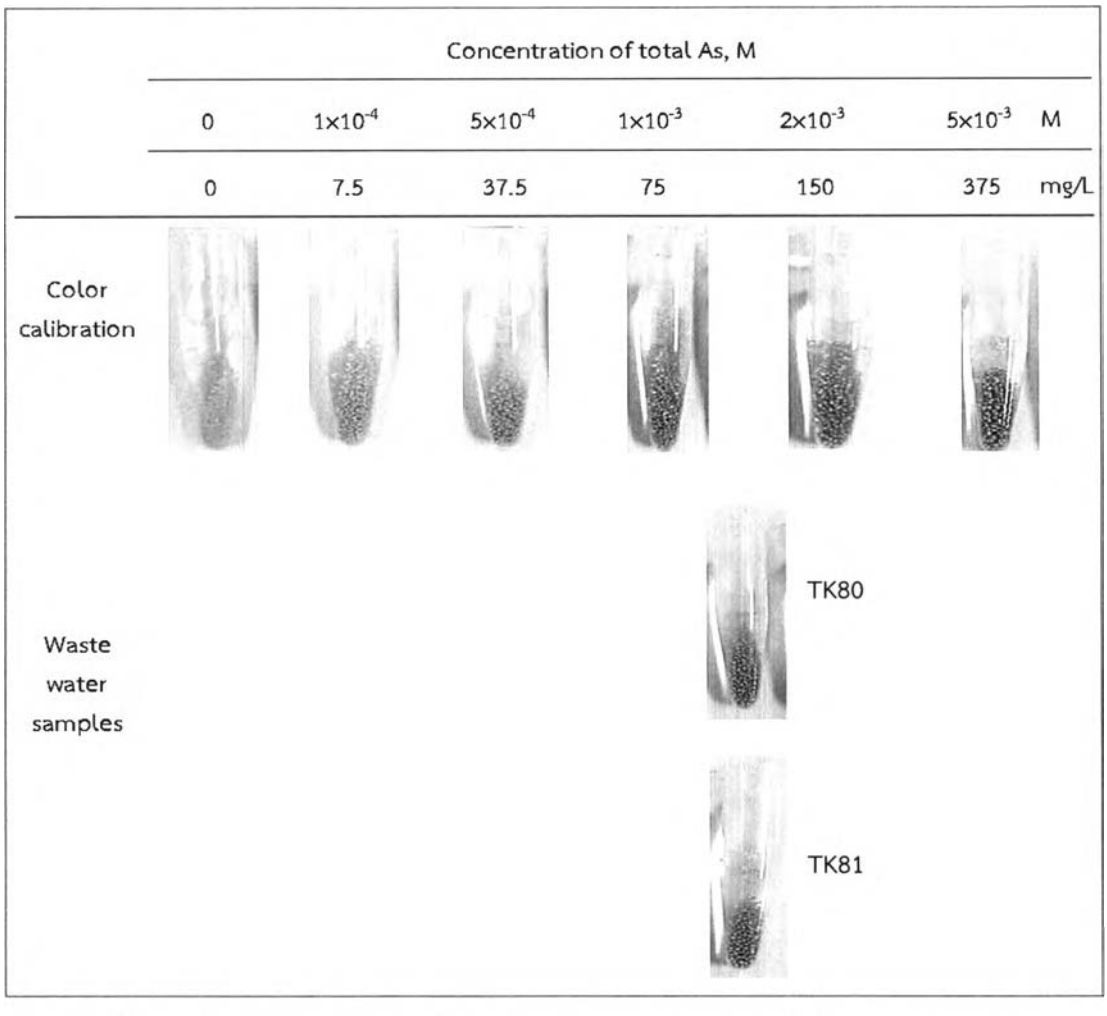


**Figure 4.25** The color of $BF_2$-curcumin-coated resin applied for the waste water samples.

**Table 4.6** The ICP-OES measurement of the waste water samples

| Waste water samples | Concentration of total As (mg/L) |
|---|---|
| TK80 | 130 ± 2 |
| TK81 | 132 ± 3 |

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