CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Chemical properties

Arsenic (As) is a semi-metal element and a well known toxic chemical. It is odorless and tasteless. Arsenic is widely used in many applications, such as pesticides, manufacturing metals and alloys, wood treatments, and refining petroleum industry [1, 2].

Arsenic can exist in four oxidation states: -3, 0, +3 and +5. These compounds are found in rock, soil, water, and air. In water, arsenic species mostly appear as oxyanions in both organic forms and inorganic forms [20-22], as shown in Figure 2.1. Inorganic forms of arsenic, arsenite (As(III)) and arsenate (As(V)) are the major species in water, whereas minor amounts of organic arsenic are commonly present as well [21].

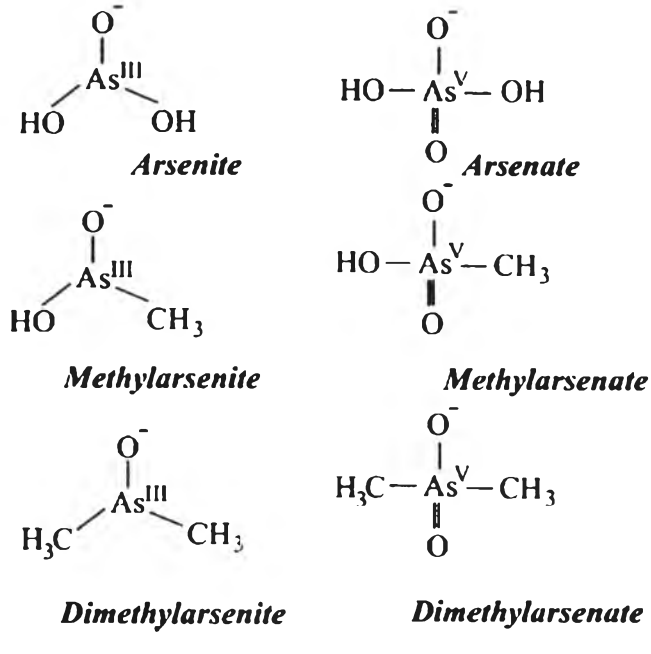


Figure 2.1 Arsenic species found in water [12].

As(III) and As(V) are present in different species depending on the pH of solution [5, 20]. The distribution of species of As(III) and As(V) are shown in Figure 2.2, and the acidic dissociation equilibrium and pK_a of those species are shown in Table 2.1 and 2.2.

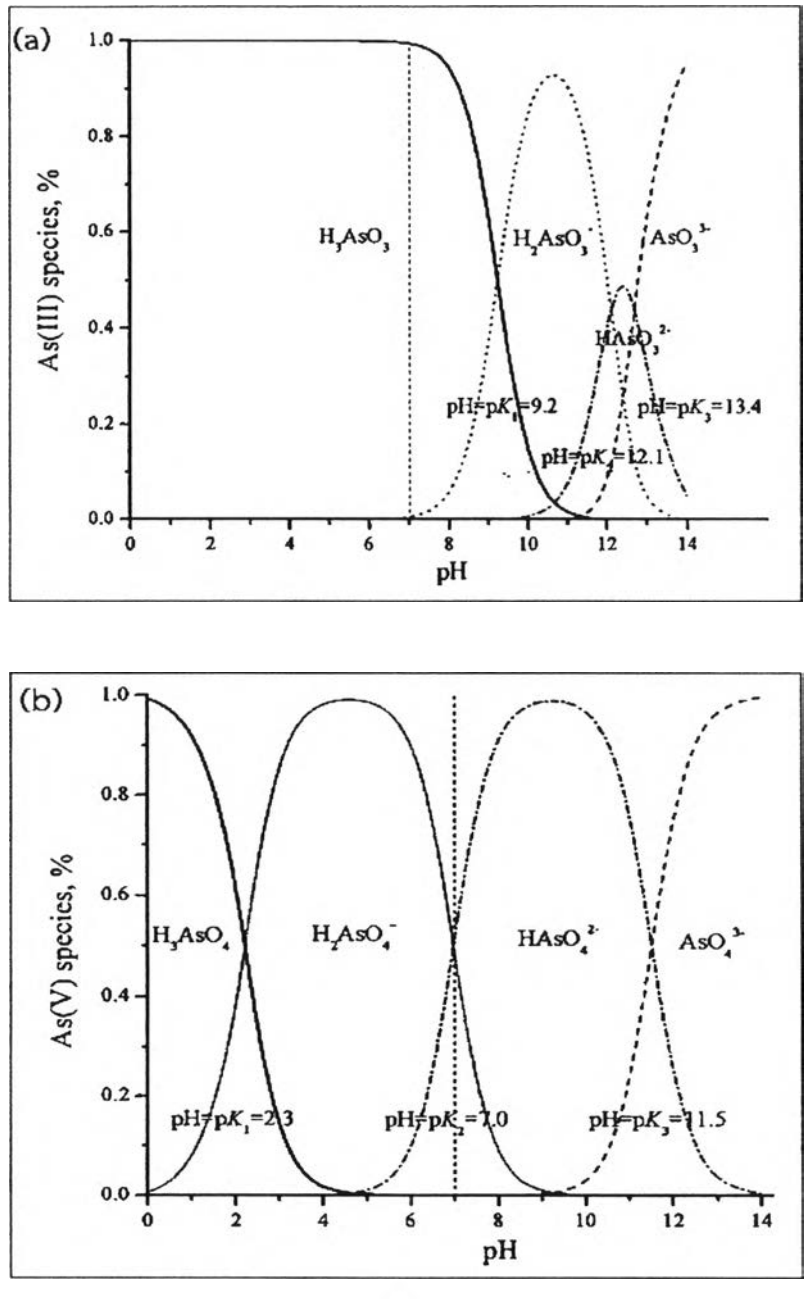


Figure 2.2 Distribution of (a) arsenite (As(III)) and (b) arsenate (As(V)) species at various pH [20, 23].

Table 2.1 Acidic dissociation reaction of As(III) species and its pKa [5]

Reaction	pK_a
$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+$	9.2
$H_2AsO_3^- \rightleftharpoons HAsO_3^{2-} + H^+$	12.1
$HAsO_3^{2-} \rightleftharpoons AsO_3^{3-} + H^+$	12.7

Table 2.2 Acidic dissociation reaction of As(V) species and its pKa [5]

Reaction	pK_a
$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+$	2.3
$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+$	6.8
$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+$	11.6

2.1.2 Toxicity of arsenic

Arsenic contamination in water is a critical environmental pollution that is partly contributed by industrial waste water. Human can be exposed to arsenic via touching, eating and drinking contaminated water. Arsenic can be harmful to human health both in short and long terms. The health effects of arsenic toxicity include dermal changes, eczema, burning and dryness of the mouth and throat, anemia, burning sensation of eyes, skin cancer, and renal cancer, or may cause mutagenesis [22, 24, 25]. Due to the extreme toxicity of arsenic, the control of arsenic quantity in waste water from industry is important. The Pollution Control Department of Thailand has regulated the amount of arsenic in waste water in Thailand at the maximum allowed concentration of 0.25 mg/L [26].

2.2 Arsenic determination

Arsenic contamination in water caused numerous damages to human and environment, thus the determination of arsenic is very important. Among the popular techniques for arsenic detection in water are spectroscopy, chromatography and electrochemistry. Some of these methods for arsenic determination are reviewed hereafter.

Spectroscopy techniques

Anthemidis *et al.* [27] proposed a simple and robust on-line sequential insertion system coupled with hydride generation atomic absorption spectrometry (HG-AAs) for As(III) and total arsenic determination. They designed an integrated reaction chamber/gas–liquid separator for the generation and transportation of arsine gas from the pre-reduction step by HCl and $NaBH_4$ solution. The detection limit of this method was 0.1 and 0.06 μg/L for As(III) and total arsenic, respectively.

Minakata *et al.* [28] developed a simple and selective method for the determination of arsenic by using electrospray ionization mass spectrometry (ESI-MS). Inorganic arsenic was reacted with a chelating agent and extracted with methyl isobutyl ketone before the aliquot of this solution was injected into the ESI-MS instrument without chromatographic separation. The limit of detection of arsenic was 0.22 μg/L.

Michon *et al.* [29] studied the optimization of graphite furnace atomic absorption spectrometry (GFAAS) method to improve the sensitivity for determination of low level arsenic in drinking water. The limit of detection of this method was 0.26 μg/L.

Xiong *et al.* [30] developed a simple, and selective method for the separation and preconcentration of inorganic arsenic (As(III)/As(V)) species by a microcolumn on-line coupled with inductively coupled plasma-optical emission spectrometry (ICP-OES). In this method, total inorganic arsenic were extracted with cetyltrimethyl-

ammonium bromide (CTAB)-modified alkyl silica sorbent, after the oxidation of As(III) to As(V) with $KMnO_4$. The limit of detection was 0.15 µg/L.

Chromatography techniques

Campillo *et al.* [31] proposed a determination method for organic arsenic and inorganic arsenic in sea water and beverages by using gas chromatography with atomic emission detector (GC-AED). They prepared the samples with a simple liquid-liquid extraction using cyclohexane before the measurement. The detection limits in seawaters and beverages were 0.05, 0.15 and 0.8 ng/mL for dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and inorganic arsenic, respectively.

Electrochemistry techniques

Salaün et al. [32] demonstrated an anodic stripping voltammetry (ASV) with gold microwire electrode for the measurement of arsenic in sea and fresh water. They suggested that this method is a sensitive speciation method for As(III) and As(V) by using a pH step to differentiate between the two species. The detection limit of this method was 0.2 nM for As(III) at pH 8 and 0.3 nM for combined arsenic (As(III)+As(V)) at pH 1.

These techniques are all sensitive and accurate for the determination of low concentration of arsenic but they all require costly instruments, high maintenances and professional skills.

2.3 Naked eye detection of arsenic

Naked eye detection is a colorimetric method that detects the changes of color or absorption wavelength of visible light of solution when the analyte interacts with ligand molecules. This technique can be detected visually or with the aid of a colorimeter: UV-visible spectrometer or fluorescence spectrometer. Naked eye detection for qualitative and quantitative analysis is applicable in both solution

system and solid system. Thus, the naked eye detection is an interesting method, and it has been studied for the determination of arsenic in aqueous solution because this technique is relatively simple, low cost and special instruments are not essential.

2.3.1 Naked eye detection in solution system

Most of the naked eye detection methods of arsenic require the formation of volatile arsine gas (AsH_3) before the measurement. These methods are partly reviewed hereafter. Gutzeit's Test [14-16] is a classic standard approach for arsenic determination based on transforming the arsenic compounds in water into arsine gas by using zinc powder or sodium borohydride under acidic condition. The arsine gas exposed to a paper impregnated with mercury(II) chloride or mercury(II) bromide generates a colored compound. The color of paper turns to yellow by a small amount of arsine and progressively turns to reddish-brown with increasing amount of arsine.

Marsh's Test [16] or Hofmann's test is another standard method for measuring arsenic in arsine form like Gutzeit's test. The arsine gas is transported through silver nitrate solution, resulting in black precipitates of silver(0) in the solution.

Other standard colorimetric methods are silver diethyldithiocarbamate spectrophotometric procedure [17]. In this procedure, arsine gas forms a colored complex with diethyldithiocarbamate which can be detected by a spectrophotometer at wavelength 500-600 nm.

Arbab-Zavar *et al.* [33] developed a method for the determination of arsine from electrochemical reduction. This arsine reacted with silver diethyldithiocarbamate to form a red complex and the absorbance of this complex was measured at 525 nm. The limit of detection was 0.05 μg/mL.

Baghel *et al.* [34] studied a rapid colorimetric method for arsenic detection by using auric chloride. Magnesium and oxalic acid were used for arsine gas

generation. The arsine was allowed to react with auric chloride on filter paper. The proposed reaction mechanisms are shown in Equation 2.1.

$$AsO_3^{3-} \text{ or } AsO_4^{3-} + Mg^0 + (COOH)_2 \longrightarrow AsH_3\,(g)$$
$$AsH_3\,(g) + AuCl_3 + H_2O \longrightarrow Au^0 + HCl + H_3AsO_3 \qquad (2.1)$$
Metallic gold (pink-violet)

The color of paper turned to pink-violet within 1 minute and the detection limit of this method was 0.05 mg/L.

Nevertheless, a major drawback of these methods was the toxicity of arsine gas that was the most poisonous arsenic species and its complicated preparation and treatment. Therefore, many researches have been developed around the naked eye detection of arsenic without the formation of arsine gas.

Lenoble *et al.* [35] demonstrated a simple molybdenum blue method for the measurement of As(V) based on the arsenomolybdate complex from the reaction between As(V) and ammonium molybdate. Then, the complex was reduced with ascorbic acid or hydrazine sulphate, the solution color of complex changed to blue in less than 1 hour at room temperature. The reaction mechanism is shown by Equation 2.2.

$$As(V) + Mo^{VI}{}_7O_{24}^{6-} \longrightarrow As^{V}Mo^{VI}{}_{12}O_{40}^{3-}$$
$$As^{V}Mo^{VI}{}_{12}O_{40}^{3-} + 4e^- \longrightarrow As^{V}Mo^{V}{}_4Mo^{VI}{}_8O_{40}^{7-} \qquad (2.2)$$
(blue)

The blue color of this complex relates to the quantity of arsenic. The detection limit of this method was 20 µg/L.

Pillai *et al.* [36] presented an alternative method for As(III) determination by using the bleaching of pinkish red color of Rhodamine-B by iodine which was released from the reaction between As(III) and potassium iodate. The

bleaching of pinkish red color of Rhodamine-B could be detected at a wavelength of 553 nm. This method was applied for determination of arsenic in the concentration range of 0.04-0.4 mg/L with a relative standard deviation (RSD) of 1.76%.

Kalluri *et al.* [37] developed a sensitive and efficient method for the determination of trace arsenic in ground water by modified gold nanoparticles with glutathione, dithiothreitol and cysteine. This method was based on the aggregation of the modified gold nanoparticles that caused the solution color change from red to blue when the solution contained both As(III) and As(V). The detection limit was 10 ng/L and was achieved within less than 10 minutes.

The previous works have shown that arsenic can be determined with good detection limit and the measurements can be carried out by either spectrophotometer or visual observation. However, such methods are not applicable for field analysis and some approaches still require the use of organic solvents.

2.3.2 Naked eye detection in solid system

The naked eye detection in solid system is an alternative technique having been recently proposed for the determination of arsenic in aqueous solution because it is simple and environmental friendly, as well as be applicable for field analysis. Solid supports useful for naked eye detection are, for example, resins [38, 39], papers [40, 41], polymers [42], and membranes [43]. Resins are widely used as solid support for naked eye detection because it is simple to modify their surface.

In 2005, Matsunaga *et al.* [44] proposed a naked eye detection of As(V) by using molybdenum loaded on a chelating resin having ß-hydroxypropyl-di(ß-hydroxyethyl) amino moiety as shown in Figure 2.3.

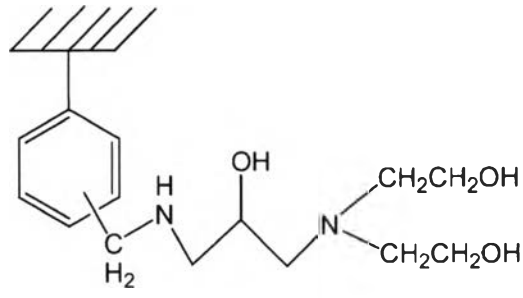


Figure 2.3 The chemical structure of chelating resin having ß-hydroxypropyl-di(ß-hydroxyethyl) amino moiety [44].

The molybdenum loaded resin reacted with As(V) and then the color of resin changed from pale yellow to greenish blue under reductive conditions using ascorbic acid (Figure 2.4). The detection limit of the method was 1×10^{-6} M or 375 µg/L.

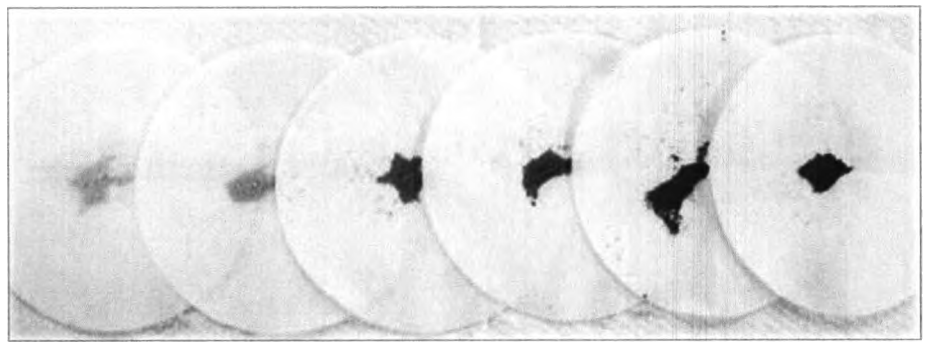


Figure 2.4 The color change of the resin with different concentrations of As(V): 0, 1×10^{-6}, 1×10^{-5}, 2×10^{-5}, 1×10^{-4}, 2×10^{-4} M, from left to right [44].

2.4 Amberlite XAD-2 resin

Amberlite XAD-2 polymeric adsorbent is a type of commercial resin that is hydrophobic cross-linked polystyrene copolymer (Figure 2.5). The unique properties of Amberlite XAD-2 resin are macroreticular porosity, broad pore size distribution and large surface area, and a chemically homogeneous nonionic structure [45, 46]. The

physical properties and structure of a hydrophobic, macroreticular Amberlite XAD-2 resin bead are shown in Table 2.3 and Figure 2.6.

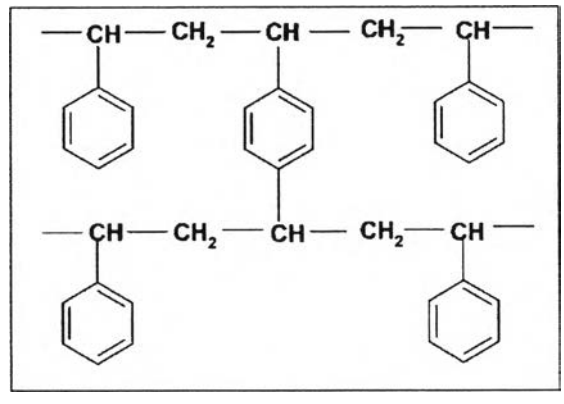


Figure 2.5 The chemical structure of Amberlite XAD-2 resin [47].

Table 2.3 Physical properties of Amberlite XAD-2 resin [46]

Physical properties	
appearance	Hard, spherical opaque beads
porosity	0.41 mL pore/mL bead
surface area	300 m^2/g
mean Pore Diameter	90 Å
true Wet Density	1.02 g/mL
skeletal Density	1.08 g/mL
bulk Density	40 lb/ft^3 (640g/L)

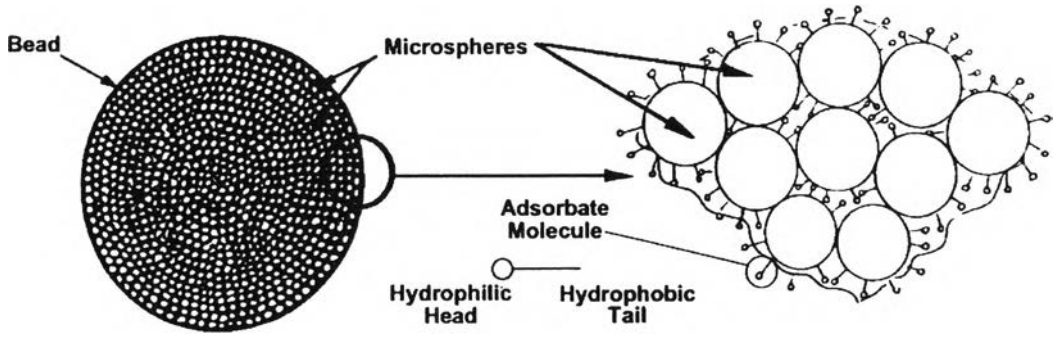
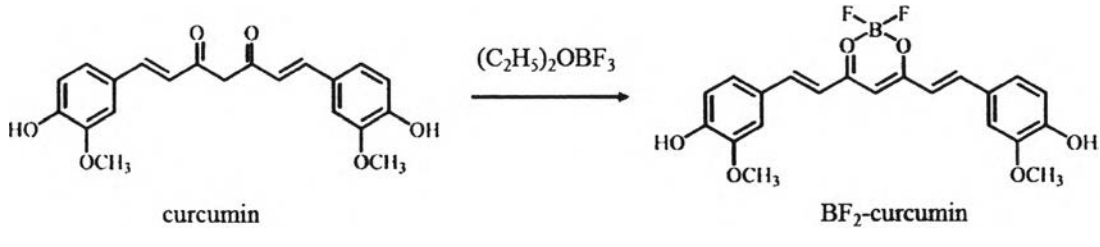


Figure 2.6 Structure of a hydrophobic, macroreticular Amberlite XAD-2 resin bead [46].

From this structure of Amberlite XAD-2, the hydrophobic part of the molecule can adsorb nonionic substances on the hydrophobic polystyrene surface of the resin, while the hydrophilic part remains oriented in the aqueous phase. Amberlite XAD-2 has been widely used for the removal of organic compound in water and also preconcentration procedures [48-51] because of its good physical and chemical properties, durability and water insolubility. Therefore, Amberlite XAD-2 resin was selected as a solid support in this research.

2.5 Difluoroboron-curcumin (BF_2-curcumin)

Chaicham *et al.* [18,19] studied the synthesis and properties of difluoroboron-curcumin (BF_2-curcumin) (Figure 2.7) by the addition of borondifluoride group on the carbonyl group in curcumin structure from extracts of turmeric.



curcumin BF_2-curcumin

Figure 2.7 The synthesis of BF_2-curcumin [19].

In the presence of cyanide, the color of this BF_2-curcumin solution changed from red to blue which can be described by the basicity of the anions and the change of the 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. Cyanide is a conjugated base of hydrocyanic acid.with a low acid dissociation constant (pKa = 9.2), thus making it a basic anion that can abstract protons from the hydroxyl groups in BF_2-curcumin molecule, and the produced negative charges delocalize to acceptor part resulting in the change of BF_2-curcumin color from red to blue. The negative charges transfer process of BF_2-curcumin after adding cyanide is shown in Figure 2.8.

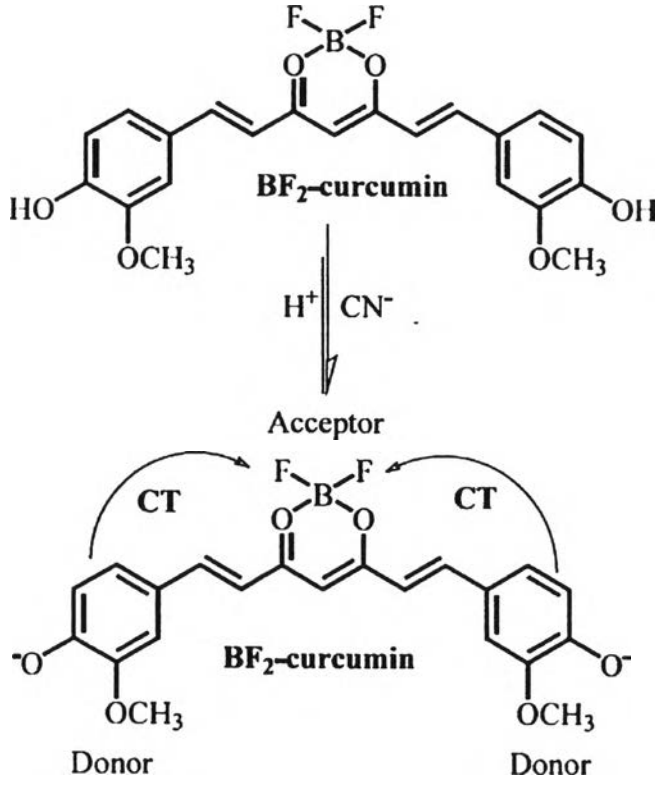


Figure 2.8 The negative charges transfer process of BF_2-curcumin after adding cyanide [18]

Arsenic in water is normally present as oxyanions with relatively low acid dissociation constants (Table 2.1 and 2.2) [5, 21], therefore, it can presumably

deprotonate the hydroxyl moiety of BF_2-curcumin molecule. The negative charges produced could then similarly delocalize to the acceptor part resulting in the change of BF_2-curcumin color.

Based on these literature reviews, this research aims to develop a new colorimetric method for the determination of inorganic arsenic in water samples by UV-visible spectrophotometry and visual observation both in BF_2-curcumin solution and BF_2-curcumin coated resin (Amberlite XAD-2).