# CHAPTER 1

# Introduction

## 1.1 Heavy metals

Heavy metals like cadmium, lead and zinc are elements found in nature and used in many industries. Cadmium has many uses, including batteries, pigments, metal coating and plastics. It is used extensively in electroplating. In the human system, cadmium can buildup in the kidney and possible cause kidney disease in long term, and can lead to lung damage and fragile bones. The Itai-Itai disease caused by cadmium exposure is well known. Lead is a highly toxic metal and related to various health concerns. It is used in several products like gasoline, cosmetic, paints and glazed pottery so possibly contaminated in air, soil and water. For the symptoms, lead can affect every organ and system in the body. Long term exposure of adults can decrease performance of nervous system, increase blood pressure and anemia. Zinc is found mostly in mining industry. The degree of toxicity of zinc is not high, but it depends on the ionic form. The daily average of zinc is 10 - 50 mg day$^{-1}$ for adult. The high dose of zinc can damage the kidneys, liver and gonads [Hubicki and kołodyńska, 2016, Human health effects of heavy metals, 2016].

Cadmium and lead are hazardous elements which have highly toxic effects on health and environment. They can accumulate in the environment and living organisms, and highly toxic even at low concentration, thus their trace analyses are very important.

## 1.2 Techniques for heavy metals determination at low concentration

Several analytical techniques have been used for heavy metals determination at trace levels such as spectrometry and electrochemistry. Generally, atomic absorption spectroscopy (AAS) [Fu *et al.*, 2013], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [Injang *et al.*, 2010], inductively coupled plasma-mass spectroscopy (ICP-MS) [Lee *et al.*, 2016] and inductively coupled plasma-optical emission spectroscopy (ICP-OES) [Armstrong *et al.*, 2010] are routine methods used widely for determination of metals. However, these techniques need well trained personal, use explosive gases like acetylene gas, use expensive gases like argon gas and must have appropriately equipped laboratory. While electrochemical technique has advantages such as economic efficiency, easy to use and can be tailored to give a wide dynamic range from low levels to ppm range or higher.

## 1.3 Anodic stripping voltammetry

### 1.3.1. Principle of anodic stripping voltammetry

Anodic stripping voltammetry (ASV) is one of electrochemical method for quantitative determination of specific ionic or non-ionic species. The voltammetric cell consists of electrolyte which is needed in order to provide electrical conductivity such as buffer solution and three electrodes including of working electrode (WE), auxiliary electrode (AE) and reference electrode (RE). The working electrode makes contact with the analyte which apply the potential in a controlled reaction for transfer of charge from analyte. The auxiliary electrode is adjusted to balance the reaction occurring at the working electrode and the reference electrode act as reference in measuring and controlling the potential of working electrode [Jakmunee, 2549].

The ASV consists of 2 steps as shown in Figure 1.1. The first step is a controlled constant potential at the working electrode to deposit the metal ions (cadmium, lead and zinc) on the electrode which the reduction reaction is taken place as shown in the equation 1.1, 1.2 and 1.3.

$$\mathrm{Cd^{2+} + 2e^{-} \rightleftharpoons Cd} \tag{1.1}$$

$$\mathrm{Pb^{2+} + 2e^{-} \rightleftharpoons Pb} \tag{1.2}$$

$$\mathrm{Zn^{2+} + 2e^{-} \rightleftharpoons Zn} \tag{1.3}$$

The second step scan the potential toward a more positive potential and the analyte is stripped from the working electrode returning to solution in its oxidized form as shown in the equation 1.4, 1.5 and 1.6. The current obtained during the stripping step is linearly proportional to the metal concentration. Following the standard reduction potentials, zinc is a stronger reducing agent than cadmium and lead, so in the stripping step zinc ions will be stripped before cadmium and lead, respectively [Jakmunee, 2549].

$$Cd \rightleftharpoons Cd^{2+} + 2e^- \qquad 1.4$$

$$Pb \rightleftharpoons Pb^{2+} + 2e^- \qquad 1.5$$

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \qquad 1.6$$

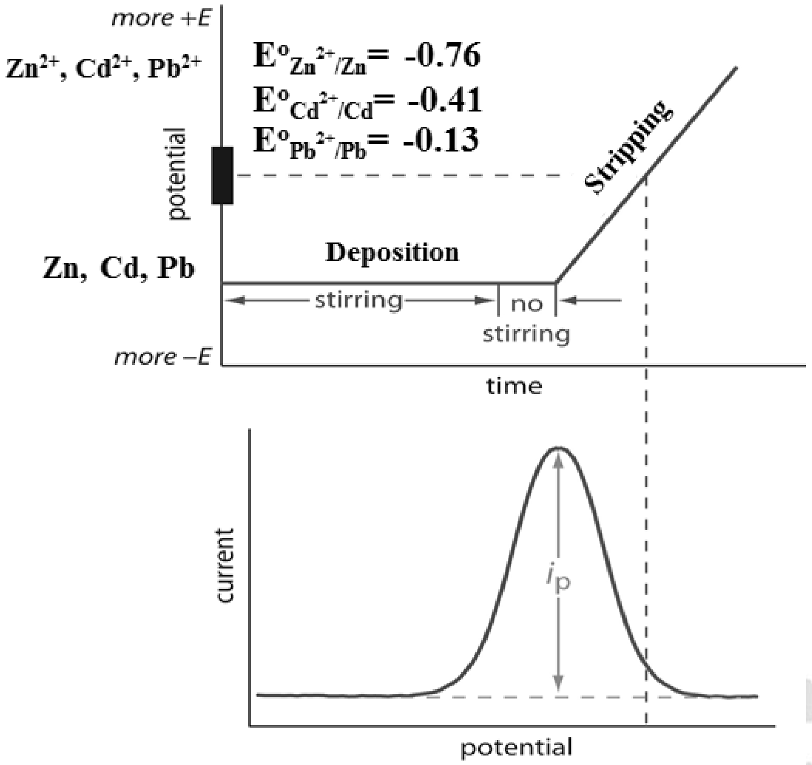


**Figure 1.1** Potential-excitation signal and voltammogram for ASV [Voltammetric method, 2016]

The ASV is a very high sensitivity technique because the deposition step on the working electrode allows pre-concentration of the metals, and the application of voltage pulses during the stripping step produce a high faradaic current and well-defined stripping peaks of different metal ions. The most common pulse wave forms used to obtain the stripping scan are differential pulse (DPASV) and square wave (SWASV).

The DPASV apply the potential pulses as shown in Figure 1.2 a) and the current is measured two times, before applying the pulse ($i_1$) and the end of cycle ($i_2$). The difference in the two currents ($\triangle i$) as shown in the equation 1.7 gives a high signal to noise ratio.

$$\triangle i = i_2 - i_1 \tag{1.7}$$

The SWASV applies the potential of alternating current pulses as shown in Figure 1.2 b) and the current is also measured twice, i.e., forward pulse ($i_1$) and reverse pulse ($i_2$), which give anodic and cathodic currents. Then the difference in the two currents ($\triangle i$) was calculated as shown in the equation 1.8. In case of reversible reaction, SWASV gives a high current signal. Thus, the SWASV has higher sensitivity than the DPASV method [Jakmunee, 2549].

$$\triangle i = i_1 - (-i_2) = i_1 + i_2 \tag{1.8}$$

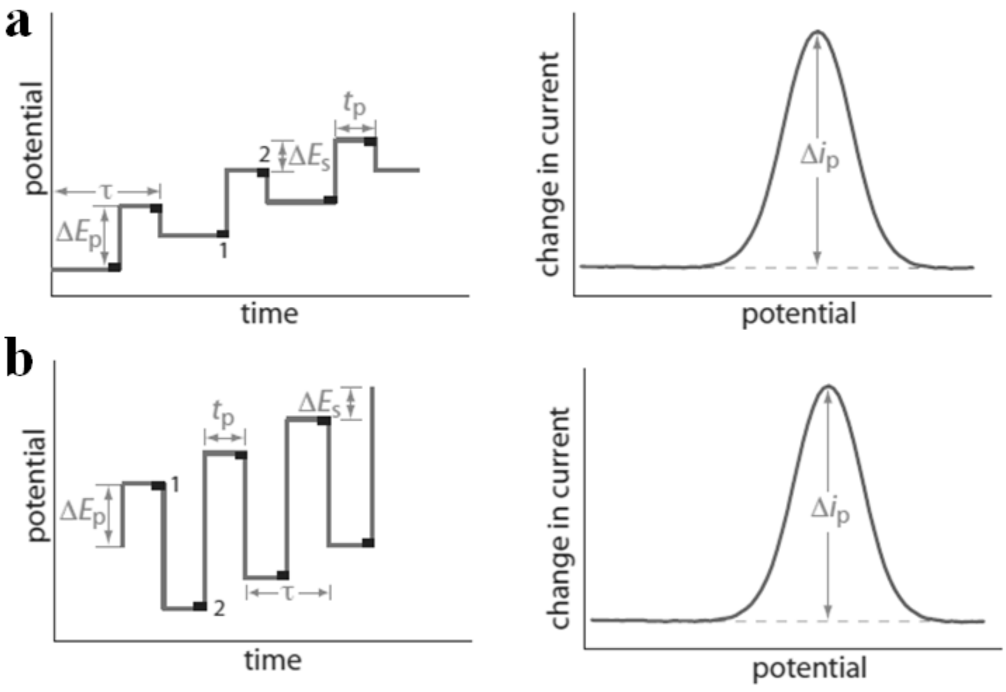


**Figure 1.2** Potential-excitation signals and voltammograms for a) differential pulse voltammetry and b) square-wave voltammetry. The symbols in the diagrams are as follows: T is the cycle time; $\triangle Ep$ is a fixed pulse potential; $\triangle Es$ is the fixed change in potential per cycle, and tp is the pulse time [Voltammetric method, 2016].

The ASV has been recognized as a powerful electroanalytical technique for trace metal measurements. Several reports showed its high sensitivity for simultaneous determination of eco-toxic metals (cadmium, lead, copper and zinc) at very low concentration levels. The method was successfully applied to real sample, such as Jakmunee and Junsomboon reported a method for determination cadmium, lead, copper and zinc ions in glazed ceramic wares leaching by 4% (v/v) acetic acid. The extract can be analyzed directly using a hanging mercury drop electrode, with the extractant solution being used as an electrolyte. The method provided detection limits of 0.25, 0.07, 2.7 and 0.5 μg $L^{-1}$ for cadmium, lead copper and zinc, respectively [Jakmunee and Junsomboon, 2008]. Zbeda *et al.* determined cadmium, lead and zinc in tap water samples using *in situ* deposited mercury film electrode on the graphene modified glassy carbon electrode. Preconcentration was carried out in 0.1 M acetate buffer solution (pH 4.6) and the detection limits were 0.05, 0.14 and 0.08 μg $L^{-1}$ for cadmium, lead and zinc, respectively [Zbeda *et al.*, 2013].

### 1.3.2 Working electrode

In traditional ASV, mercury film and hanging mercury drop have been widely used as working electrode materials, because they provide high sensitivity and a large negative potential range that is suitable for determination of the analyte metals. For electrochemical analysis, mercury was used due to the high overpotential of hydrogen on this electrode that allows its use at the useful negative potential (Figure 1.3).

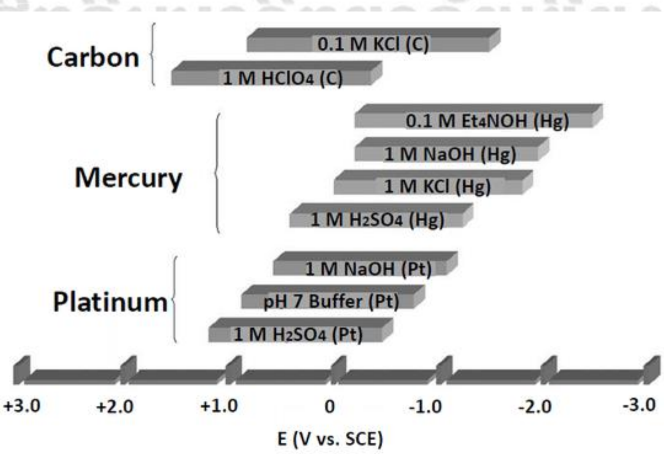


**Figure 1.3** Potential window of carbon, mercury and platinum electrodes in an aqueous solution [Barón-Jaimez *et al.*, 2013]

On the other hand, mercury is very toxic and posses a significant health and environmental hazard. A variety of other electrode materials have been consequently investigated as possible alternatives to mercury (Figure 1.4) such as noble metals (platinum, gold and silver) and others (bismuth, carbon, boron-doped diamond and antimony). In my work, I am interested in a greener method development, I have chosen bismuth electrode because it avoids the use of toxic mercury electrode.

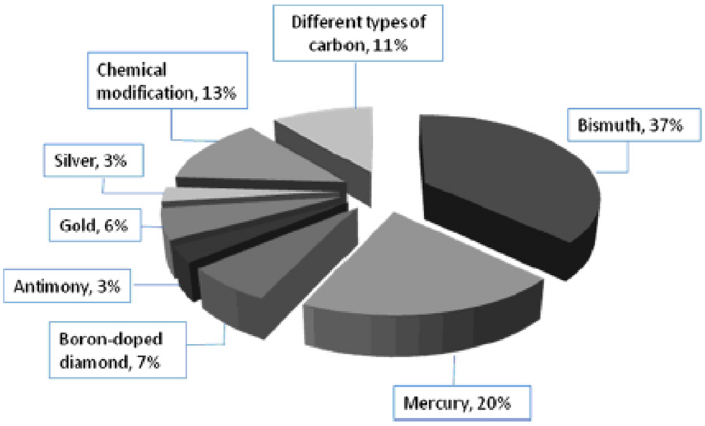


**Figure 1.4** The percentage of lead sensors based on different materials [Arduini *et al.*, 2010]

### 1.3.3 Bismuth film working electrode

Many studies have demonstrated the applicability of bismuth film electrode (BiFE) as a possible alternative working electrode for determination of trace heavy metals with electroanalytical behavior similar to that of mercury based electrodes. The modification of an electrode by bismuth film is based on electroplating a film of bismuth onto the surface of a supported electrode. Bismuth forms a fused alloy with some heavy metals as shown in the equation 1.9. This process can be divided in two different ways, i.e. *ex situ* and *in situ* plating method.

$$\mathrm{Bi} + \mathrm{M}^{n+} + \mathrm{ne}^- \rightleftharpoons \mathrm{Bi(M^0)} \qquad 1.9$$

In preparing bismuth film electrode by *ex situ* plating method, the substrate electrode is immersed into a bismuth(III) solution, after the application of an appropriate potential for electrodeposition, bismuth(III) ions are reduced to metallic bismuth and electroplated on the electrode surface. Then, the bismuth film electrode is carried out to sample solution for metal determination. In the *in situ* plating method, bismuth(III) ions are directly added to the sample solution and electrochemically deposited on the electrode surface together with the analyte metals during the analysis [Arduini *et al.*, 2010].

ASV measurements with *in situ* bismuth plating is simpler, which bismuth(III) ions are directly added into the sample solution, so the many choices of supported electrodes are applied such as carbon nanotube, glassy carbon, activated carbon, graphite [Hwang *et al.*, 2008], screen-printed electrode [Injang *et al.*, 2010], glassy carbon electrode [Chen *et al.*, 2012], graphene oxide-SPE [Fu *et al.*, 2013 and Ping *et al.*, 2014], activated graphene [Lee *et al.*, 2015], and ionic liquid-graphite [Zhang *et al.*, 2016] as summarized in Table 1.1. The *in situ* bismuth plating also provides more advantage than the *ex situ* one. Zhang *et al.* compared the bismuth film modification with *in situ* and *ex situ* method for determination of cadmium and lead. They found that *in situ* procedure give higher sensitivity while the *ex situ* modified bismuth film electrode was stored at room temperature for 24 h, the current response of lead decreased about 18%, resulting from the natural oxidation of bismuth in the air due to its instability [Zhang *et al.*, 2016]. Quintana *et al.* have reported the same that the *in situ* bismuth film electrode can produce better analytical sensitivity than *ex situ* bismuth film electrode [Quintana *et al.*, 2011].

Moreover, the different modifications of bismuth electrode in the literature such as bismuth oxide [Riman *et al.*, 2015], bismuth bulk [Armstrong *et al.*, 2010], bismuth xerogel [Dimovasilis and Prodromidis, 2013], sputter of bismuth [Sosa *et al.*, 2014] and bismuth nanocomposite [Lee *et al.*, 2016] are summarized in Table 1.1. As in case of Sosa *et al.* who compared different methods for preparation of bismuth electrode including *in situ*, *ex situ*, bismuth oxide ($Bi_2O_3$) and bismuth sputtered modified on SPE for determination of cadmium and lead in groundwater sample. The results demonstrated that, sensitivity of bismuth *in situ* modified on SPE is the highest (Table 1.2), and voltammograms for simultaneous determination of cadmium and lead were exhibited the sharpest and the highest peak current as shown in Figure 1.5 [Sosa *et al.*, 2014].

**Table 1.1** Some researches which using ASV with various types of bismuth modified electrode for determination of cadmium, lead and zinc

| **No.** | **Substrate electrode** | **Electrode modification with bismuth** | **Technique** | **Sample** | **Detection limit (µg L$^{-1}$)** | **Linear range (µg L$^{-1}$)** | **Ref.** |
|---|---|---|---|---|---|---|---|
| **1** | Carbon nanotube/glassy carbon/Activated carbon/Graphite | *in situ* | SWASV | Water | Cd 0.7<br>Pb 1.3 | 2 - 18 and 20 - 100 | [Hwang *et al.*, 2008] |
| **2** | SPE | *in situ* | SIA-ASV | Herb | Cd 0.8<br>Pb 0.2<br>Zn 11 | 2 - 100<br>2 - 100<br>12 - 100 | [Injang *et al.*, 2010] |
| **3** | Glassy carbon electrode | *in situ* | SWASV | Tap, spring and river water | Cd 0.04<br>Pb 0.05 | 0.1 - 20<br>0.1 - 30 | [Chen *et al.*, 2012] |
| **4** | Graphene oxide-SPE | *in situ* | DPAVS | Water | Cd 0.042<br>Pb 0.089 | 0.5 - 120 | [Fu *et al.*, 2013] |
| **5** | Activated graphene | *in situ* | DPAVS | Tap water | Cd 0.07<br>Pb 0.05<br>Zn 0.57 | 5 - 100 | [Lee *et al.*, 2015] |

**Table 1.1** (Continued)

| **No.** | **Substrate electrode** | **Electrode modification with bismuth** | **Technique** | **Sample** | **Detection limit (μg L$^{-1}$)** | **Linear range (μg L$^{-1}$)** | **Ref.** |
|---|---|---|---|---|---|---|---|
| **7** | SPE | Bismuth oxide | SWASV | Tap water | Cd 0.2<br>Pb 0.2 | 0 - 12 | [Riman *et al.*, 2015] |
| **8** | - | Bismuth bulk | SWASV | river water | Cd 0.054<br>Pb 0.093<br>Zn 0.396 | 10 - 100 | [Armstrong *et al.*, 2010] |
| **9** | Glassy carbon electrode | Bismuth xerogel | SWASV | Tab, table and lake water | Cd 0.37<br>Pb 1.3 | 0.56 - 11.24<br>1.04 - 20.72 | [Dimovasilis and Prodromidis, 2013] |
| **10** | SPE | Sputter of bismuth | DPAVS | Certified groundwater | Cd 0.10<br>Pb 0.16 | 0.33 - 12.3<br>0.53 - 19.8 | [Sosa *et al.*, 2014] |
| **11** | Graphene oxide-glassy carbon electrode | Bismuth nanocomposite | DPASV | Tap water | Cd 0.18<br>Pb 0.11<br>Zn 1.80 | 1 - 100 | [Lee *et al.*, 2016] |

**Table 1.2** Calibration data for simultaneous determination of cadmium and lead on different Bi-SPEs [Sosa *et al.*, 2014]

| **Electrodes** | **Cadmium** | | **Lead** | |
|---|---|---|---|---|
| | **Regression** | **$R^2$** | **Regression** | **$R^2$** |
| *in situ* Bi-SPE | Y = 6.62x + 2.14 | 0.9991 | Y = 7.17x + 11.27 | 0.9998 |
| *ex situ* Bi-SPE | Y = 2.78x – 3.30 | 0.9998 | Y = 3.53x + 4.33 | 0.9999 |
| $Bi_2O_3$ bulk SPE | Y = 3.52x – 7.12 | 0.9999 | Y = 5.14x + 29.59 | 0.9998 |
| sputtered Bi-SPE | Y = 0.78x + 0.18 | 0.9999 | Y = 3.03x + 0.47 | 0.9998 |

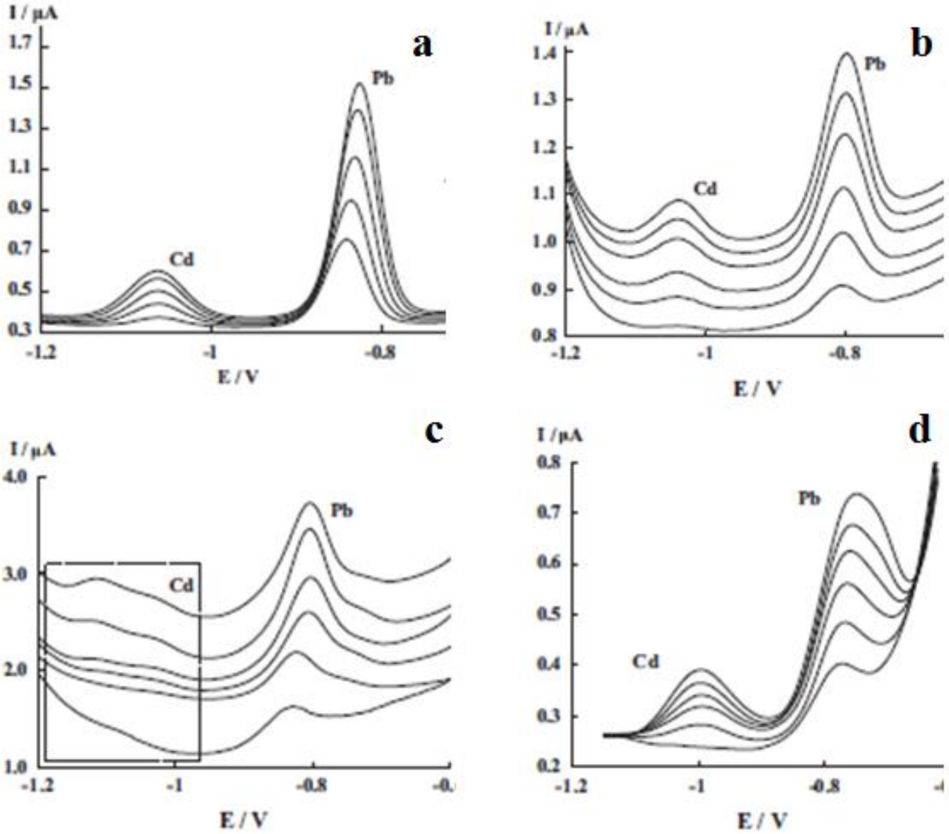


**Figure 1.5** The Voltammograms of cadmium and lead in groundwater sample on a) *in situ* Bi-SPE, b) *ex situ* Bi-SPE, c) $Bi_2O_3$ bulk SPE and d) sputtered Bi-SPE [Sosa *et al.*, 2014]

According to above, one alternative electrode is the bismuth film electrode (BiFE) which has many advantages, so I am interested in using bismuth *in situ* plating method because it provides simple preparation, high sensitivity, wide potential window, the ability to form alloys with many metals, and environmental friendly. Moreover, bismuth can be deposited on different materials such as screen-printed electrode, which is used as an economical substrate.

### 1.3.4 Screen-printed electrodes

Screen-printed electrodes (SPEs), which are used as economical electrochemical substrates, can be mass-produced in laboratory at low cost and its surface can be easily modified with different materials such as bismuth to improve property of the electrodes. Furthermore, SPE combined with ASV technique has advent of electrochemical sensor because they are disposable, inexpensive, sensitive and accurate determination of heavy metals in the field of environmental monitoring [Li *et al.*, 2012].

Over the past few decades, Bi-SPEs have been used for the analysis of cadmium, lead and zinc in wastewater [Rico *et al.*, 2008], water samples [Quintana *et al.*, 2011, Lezi *et al.*, 2012, Paukpol and Jakmunee, 2016] and glazed ceramic wares [Mandil and Amine, 2009] (Table 1.3). These works are based on the *in situ* electrochemical deposition of bismuth on SPE. This work interested in bismuth film *in situ* coated on screen-printed carbon working electrode for the simultaneous determination of cadmium, lead and zinc in extracted solution of glazed ceramic wares and treated water samples. The developed electrode is more environmentally friendly than the mercury electrode and more economical than commercial SPCE electrodes.

**Table 1.3** Some researches which using ASV with Bi-SPE for determination of cadmium, lead and zinc

| **No.** | **Sample** | **Technique** | **Limit of detection (µg $L^{-1}$)** | **Linear range (µg $L^{-1}$)** | **Additional information** | **Ref.** |
|---|---|---|---|---|---|---|
| **1** | Tap water and Wastewater | SWASV | Cd 3.6<br>Pb 2.5<br>Zn 8.2 | 10 - 100 | *in situ* bismuth modified on commercial screen-print graphite electrode | [Rico *et al.*, 2008] |
| **2** | Ceramic | SWASV | Pb 4 | Pb 5 - 80 | *in situ* bismuth modified Nafion based on screen-print graphite electrode | [Mandil and Amine, 2009] |
| **3** | Tap water | SWASV | Pb 0.15 | 0.5 -100 | *in situ* bismuth modified on screen-print graphite electrode | [Quintana *et al.*, 2011] |
| **4** | Tap, lake water | DPASV | Cd 2.1<br>Pb 1.2 | 10 - 80<br>5 - 40 | *in situ* bismuth modified on screen-print graphite electrode | [Lezi *et al.*, 2012] |
| **5** | River water | SWASV | Cd 1.7<br>Pb 0.7 | 5 - 40<br>2 - 40 | *in situ* bismuth modified on screen-print carbon electrode | [Paukpol and Jakmunee, 2016] |

## 1.4 Treatment of water

Environmental pollution can be caused by toxic metals in water especially waste water from laboratory and industry may release heavy metal ions into the environment. Therefore water contains cadmium, lead and zinc ions at concentration higher than the regulated limit must be treated before discharging into natural water. The permissible limits according to Thai standard are 0.03 mg $L^{-1}$of cadmium, 0.2 mg $L^{-1}$ of lead, and 5 mg $L^{-1}$ of zinc, respectively [Industrial effluent standard, 2539].

In this work, the chelating ion exchange method was used for removal of cadmium, lead and zinc from wastewater with Chelex 100 resin due to its high selectivity and low cost. The Chelex 100 resins consist of the iminodiacetic functional group for adsorption of metal cations. The chelating resin is efficiently operated and regenerated by adjusting pH. At very low pH, the resin acts as anion exchanger by the nitrogen atom and the two carboxylic groups are protonated. At pH about 12, the nitrogen atom and the two carboxylic groups are deprotonation. For medium pH, the resin behaves as an amphoteric ion exchanger according to Figure 1.6. The iminodiacetate groups provide electron pairs for binding the alkali metal like sodium ion. Then, the iminodiacetate groups can readily interact with heavy metal ions to form a stable coordination covalent bond as shown in equation 1.10 [Hubicki and kołodyńska, 2016].

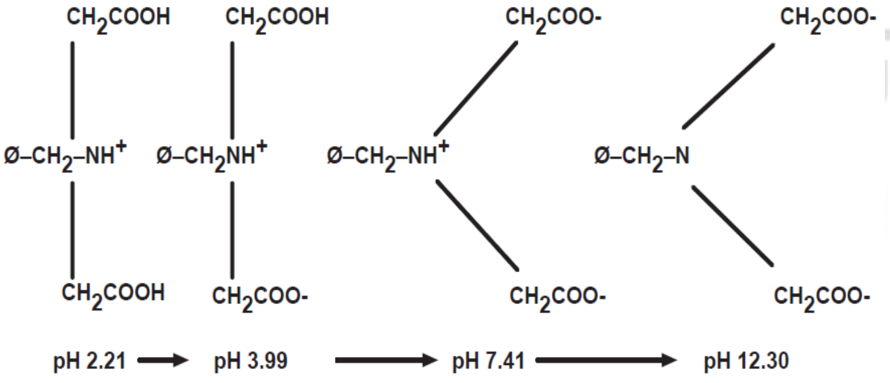
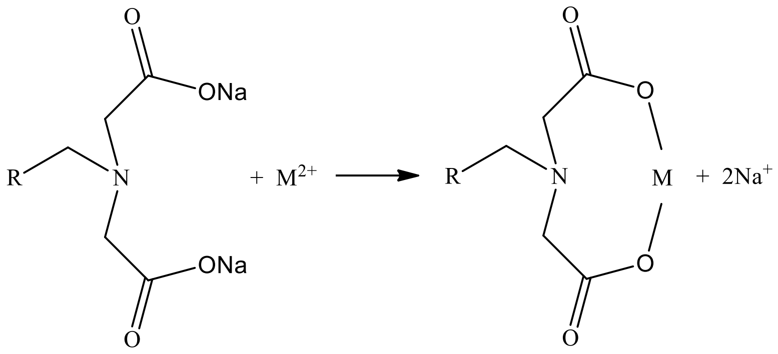


**Figure 1.6** Change in structure of Chelex 100 resin with increasing pH [Bio-Rad Laboratory, 2016]



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## 1.5 Ceramic ware

As well known, cadmium and lead are very toxic metals. These metals are found in glazed ceramic surface. Glaze is a thin shiny layer on ceramic ware. It was produced from a coating solution containing cadmium and lead, and after firing at very high temperature it was become a hard and shiny layer of cadmium and lead compounds. If the firing temperature is not high enough, it is possible to release cadmium and lead into the food [Jakmunee and Junsomboon, 2008, Mandil and Amine, 2009]. The Thai industrial standard has fixed the maximum allowable concentration limits of 0.07 mg dm$^{-2}$ for cadmium and 0.80 mg dm$^{-2}$ for lead in ceramic ware [Thai industrial standard, 2546].

## 1.6 Research objectives

1.6.1 To develop ASV method with Bi-SPCE as a working electrode for determination of cadmium, lead and zinc at trace concentration level

1.6.2 To apply the developed method for real sample analyses, such as treated water samples and glazed ceramic ware samples