การสกัดตะกั่วในน้ำด้วยเฟสของแข็งโดยใช้เรซินที่ดัดแปรด้วยไตรเอทิลีนเททระมีน สำหรับการตรวจวัดด้วยยูวี-วิสิเบิลและอะตอมมิกสเปกโทรเมตรี

นางสาวณัฏฐิกา งามกิจภิญโญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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SOLID PHASE EXTRACTION OF LEAD IN WATER USING TRIETHYLENETETRAMINE-MODIFIED RESIN FOR DETERMINATION BY UV-VISIBLE AND ATOMIC SPECTROMETRIES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry
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Thesis Title	SOLID PHASE EXTRACTION OF LEAD IN WATER USING TRIETHYLENETETRAMINE-MODIFIED RESIN FOR DETERMINATION BY UV-VISIBLE AND ATOMIC SPECTROMETRIES
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ณัฏฐิกา งามกิจภิญโญ : การสกัดตะกั่วในน้ำด้วยเฟสของแข็งโดยใช้เรซินที่ดัดแปรด้วยไตรเอทิลีนเททระมีนสำหรับการตรวจวัดด้วยยูวี-วิสิเบิลและอะตอมมิกสเปกโทรเมตรี. (SOLID PHASE EXTRACTION OF LEAD IN WATER USING TRIETHYLENETETRAMINE-MODIFIED RESIN FOR DETERMINATION BY UV-VISIBLE AND ATOMIC SPECTROMETRIES) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร.อภิชาติ อิ่มยิ้ม, 65 หน้า.

พอลิสไตรีนไดไวนิลเบนซีนที่มีหมู่ไตรเอทิลีนเททระมีนเตรียมโดยปฏิกิริยา 2 ขั้นตอนสำหรับใช้เป็นตัวดูดซับในการสกัดตะกั่วในน้ำด้วยเฟสของแข็งก่อนการวิเคราะห์ด้วยยูวี-วิสิเบิลและเฟลมอะตอมมิกแอบซอร์พชันสเปกโทรเมตรี เฟสของแข็งที่เตรียมได้มีความสามารถในการสกัดที่จำเพาะกับตะกั่วในสารละลายตะกั่วและสารละลายโลหะผสม (ตะกั่วกับโลหะชนิดอื่นได้แก่ โคบอลต์ โครเมียม ทองแดง นิกเกิล และสังกะสี) ไม่แตกต่างกัน เวลาที่เหมาะสมในการสกัดตะกั่วเท่ากับ 60 นาทีในระบบแบทช์ อันดับในการดูดซับของตะกั่วเป็นการดูดซับอันดับที่สอง ค่าความจุสูงสุดสำหรับการดูดซับคำนวณจากสมการแลงเมียร์ได้ 4.04 ไมโครโมลต่อกรัมเฟส ภาวะที่เหมาะสมในการชะตะกั่วสำหรับการตรวจวัดด้วยเฟลมอะตอมมิกแอบซอร์พชันสเปกโทรเมตรี คือใช้สารละลายกรดไนตริก 10 เปอร์เซ็นต์เป็นตัวชะ ในเวลา 30 นาที ขณะที่สภาวะที่เหมาะสมในการชะตะกั่วสำหรับการตรวจวัดด้วยยูวี-วิสิเบิลสเปกโทรเมตรี คือ ใช้สารละลายไดไทโซนอิ่มตัวในสารละลายไตรตัน-เอกซ์ ร้อยเข้มข้นร้อยละ 7 และควบคุมพีเอชด้วยสารละลายบัฟเฟอร์แอซีเตต วิธีการนี้สามารถประยุกต์เพื่อสกัดตะกั่วในน้ำชะปูนซีเมนต์โดยมีร้อยละการได้กลับคืนในช่วง 81-84 และ 81-86 สำหรับการตรวจวัดด้วยเฟลมอะตอมมิกแอบซอร์พชันสเปกโทรเมตรีและยูวี-วิสิเบิลสเปกโทรเมตรี ตามลำดับ มีค่าเบี่ยงเบนมาตรฐานสัมพัทธ์สำหรับการตรวจวัดด้วยเฟลมอะตอมมิกแอบซอร์พชันสเปกโทรเมตรีและยูวี-วิสิเบิลสเปกโทรเมตรีเท่ากับ 2.19 และ 2.58 เปอร์เซ็นต์ ตามลำดับ ผลการสกัดด้วยระบบคอลัมน์แสดงให้เห็นว่าเฟสของแข็งไม่เหมาะสำหรับการนำไปใช้เนื่องจากมีร้อยละการสกัดต่ำอยู่ในระดับที่ไม่น่าพอใจ เฟสของแข็งหลังการสกัดไม่สามารถนำกลับมาใช้ซ้ำได้

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NUTTIGAR NGAMKITPINYO: SOLID PHASE EXTRACTION OF LEAD IN WATER USING TRIETHYLENETETRAMINE-MODIFIED RESIN FOR DETERMINATION BY UV-VISIBLE AND ATOMIC SPECTROMETRIES. ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D, 65 pp.

Polystyrene-divinylbenzene contained triethylenetetramine (TETA-PS-DVB) was successfully prepared by two step reaction and employed as sorbent in solid phase extraction (SPE) of Pb(II) before its determination by UV-visible spectrometry and flame atomic absorption spectrometry (FAAS). The sorption performance of Pb(II) in single metal solution was similar to that obtained by binary metal solutions (Pb(II) with Co(II), Cr(II), Cu(II), Ni(II), and Zn(II)) indicating the high selectivity of the sorbent. Under optimal conditions, 60 minutes were utilized for adsorption of Pb(II) on the sorbent in batch method and the kinetics of sorption fitted well with pseudo-second order rate. The maximum sorption capacity calculated from Langmuir adsorption isotherm was found to be 4.04 μmol/g. The suitable desorption solution and elution time for determination by FAAS were 10% (v/v) HNO_3 and 30 minutes, respectively. While, the determination by UV-visible spectrometry was successful using saturated dithizone in 7% (v/v) Triton X-100 solution and controlling the pH at 5.5 by acetate buffer solution. The method could be applied for the extraction of Pb(II) in cement-base leachate with the percentage recoveries of 81 to 84 and 81 to 86 for determination by FAAS and UV-visible spectrometry, respectively. The relative standard deviation for determination by FAAS and UV-visible spectrometry were 2.19 and 2.58 %, respectively. The extraction in column method showed unsatisfied low extraction percentage suggesting that the solid phase was not suitable for using in column mode. The used solid phase was unable to be reused.

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Student's Signature
Advisor's Signature

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Finally, the usefulness of this research, I dedicate to my father, my mother, and all the teachers who have taught me since my girlhood.

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LIST OF ABBREVIATIONS

ATR-FTIR	attenuated total reflectance Fourier transform infrared spectrometry
°C	degree Celsius
cm^{-1}	unit of wavenumber
CHO-PS-DVB	aldehydric polystyrene-divinylbenzene
Cl-PS-DVB	chloromethylated polystyrene-divinylbenzene
ETAAS	electrothermal atomic absorption spectrometry
FAAS	flame atomic absorption spectrometry
HSAB	hard soft acid base
ICP-OES	inductively coupled plasma optical emission spectrometry
PS-DVB	polystyrene-divinylbenzene
R^2	regression correlation coefficient
rpm	round per minute
RSD	relative standard deviation
SD	standard deviation
SPE	solid phase extraction
TETA	triethylenetetramine
TETA-PS-DVB	polystyrene-divinylbenzene containing triethylenetetramine
UV-vis	UV-visible spectrometry

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Lead is a heavy metal that is naturally found in small amounts. Currently, utilization of many products in daily life such as battery, solder, paint pigments, phosphate fertilizer, plastic stabilizer, and combustion of fossil fuel is the causes of contamination and accumulation of lead in our environment. Because lead is a very poisonous metal, it causes many health problems such as a growth inhibition and brain dysfunction in children, destructions of the central and the end of nervous connections especially in young children. Additionally, it causes weakness in fingers, wrists and ankle, and also affects on gastrointestinal tract, blood, urology, and ultimately death. Then, the determination of lead in various products should be taken into account [1, 2].

However, there are many difficulties to directly determine a trace level of lead owing to matrix interferences in real samples and lower concentration of lead than the limit of quantitation of instruments used. With this respect, a separation or preconcentration step before the measurement step is required. Several methods have been widely applied for the preconcentration such as ion exchange, coprecipitation, solvent extraction, electrodeposition, membrane extraction, and solid phase extraction, etc. [3-21].

Solid phase extraction (SPE) is one of the most generally used methods for preconcentration or extraction step because there are several advantages for example, it has a good efficiency for removing a heavy metal from their matrices, and it can easily remove the sorbent from the solution. Furthermore, with the benefits of various sorbents, selectivity, significant decrease in the amount of organic solvents, low cost, less labor and time, high concentration factor, and potential for automation, SPE is widely used for separation.

Polystyrene-divinylbenzene (PS-DVB) copolymers, commonly used as polymeric sorbent in SPE, have hydrophobic characters but they are non-selective towards lead ions resulting in difficulties for co-extraction from interferences. However, they have broader pH stability range than silica and can be often overcome their selectivity by chemical modification of their surface.

In this research, chloromethylated styrene-divinylbenzene copolymers modified with triethylenetetramine (TETA) was chosen as sorbent in SPE for extraction and preconcentration of Pb(II) ions in aqueous solution in order to accurately determine lead concentration. The selection criteria of the solid sorbent was due to its selectivity towards Pb(II) as previously reported by Nutthanara et al. [21] (the detail will be discussed in section 2.6).

1.2 Objective and scope of this research

The scope of this research was firstly to prepare polystyrene-divinylbenzene containing triethylenetetramine (TETA-PS-DVB) as SPE sorbent for Pb(II) extraction and preconcentration in aqueous sample prior to the measurement. Then, the products for each step were characterized by attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR) and ninhydrin test. Afterwards, the influences of experimental parameters for sorption and desorption of Pb(II) were investigated and followed by the determination using flame atomic absorption spectrometry (FAAS) and UV-visible spectrometry (UV-vis).

1.3 Benefit of this research

A method for extraction of Pb(II) in aqueous sample for accurate determination by FAAS and/or UV-vis will be achieved.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Metal ions extraction

Separation of analyte species from potential components is necessary in numerous fields to enhance sensitivity and extend the use of instrument. Various techniques such as solvent extraction, precipitation, solid phase extraction were used for isolation of elements from their major impurity. Two commonly employed techniques are reviewed below [22, 23].

Solvent Extraction

Solvent extraction is an extractive method based on distribution of elements between two insoluble liquid mediums: aqueous and organic solvent. The extraction performance can be enhanced by choosing additives such as ion pair or chelating agents, or salts for improving salting out effect and compromising pH of sample. It is simple but has many proprietary limitations including tedious, large amount of toxic organic solvent, emulsion formed between water and organic interface, and un-successive extraction.

Precipitation

Precipitation is a separation method that an analyte is formed with a precipitant as a precipitate and then filtered from the sample solution. Precipitation method is a sample preparation based on the difference in solubility of each component. The significant characteristics of precipitant are that it should selectively react with the target analyte, the precipitate shall be easily isolated from the solution, and has high stability.

2.2 Solid phase extraction

Solid phase extraction (SPE) is a popular sample preparation method. It could quantitatively not only exhaustively separate analyte from matrices solution but also recover in elution step. Consequently, it is extremely significant for chemical analysis of a trace level of analyte and high concentration of matrices interfering in samples for avoiding measurement uncertainty. And analytical separation is an important step for many fields of determination work. The objectives of solid phase extraction are preconcentration, clean up, and solvent exchange.

Benefits of SPE method over solvent extraction are high selectivity, good separation efficiency, ease for removal of the sorbent from the sample solution, completely free of emulsion, less labor, and low amount of organic solvent.

2.2.1 Principle

SPE is the preparation technique base on the distribution of the analyte in bulk solution and solid sorbent. The sorbates (or analytes) can be separated from sample matrices into sorbent (or solid phase) on account of their greater affinity for the solid sorbent than the sample impurities. On the contrary, in some analytical procedures, sample matrices are retained on the solid phase and the analyte remains in the sample solution.

The equilibrium of the analyte distribution is explained by distribution coefficient (K_D) [24]. It was defined to present a ratio of concentration of retained analyte on the sorbent to dissolve or suspend analyte in sample solution. And it is described by Equation 1. A high value of K_D is expected for good extraction.

$$K_D = \frac{A_s}{A_{aq}} \qquad (1)$$

where A_s is the concentration of analyte retained on the sorbent (mol L^{-1})

A_{aq} is the residual concentration of analyte in the solution at equilibrium (mol L^{-1})

2.2.2 The basic steps

Commonly, sorptive processes in SPE method comprise of four steps: conditioning, loading, washing, and elution [25, 26], as presented in Figure 2.1.

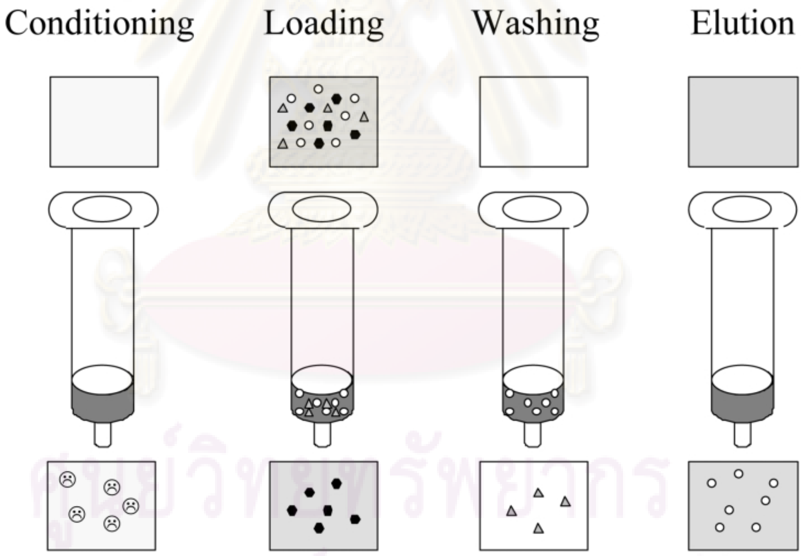


Figure 2.1 Four steps of SPE. [26]

Firstly, the sorbent is prewashed with solvent to remove impurities and solvate active sites of the sorbent. Poor sorption efficiency will be obtained if the sorbent is dried before loading step finished. Then, reconditioning must be done. Secondly, the sample solution is applied to the sorbent and the analyte is retained on the sorbent. Next, the sorbent is washed by low affinity appropriate solvent to eradicate undesired species while the analyte is not stripped. Finally, high affinity solvent is applied to strip the analyte from the sorbent for determination.

2.2.3 Retention mechanism

Retention mechanism was classified into various modes based on interactions between sorbate and sorbent [26-28]. On the contrary, retention of trace elements is classified into four modes: adsorption, chelation, ion-pairing, and ion exchange.

Adsorption

Adsorption is the mechanism that has competition between solute and solvent to adsorb onto the sorbent surface based on Van der Waals forces or hydrophobic interaction. The retention of sorbate is affected by three factors: polarity of sorbate and activity site of sorbent, surface area, and sorbent pore diameter.

Chelation

Chelation is a process that metal ions form complex with ligands containing electron donor atom (is called chelating agent) including nitrogen (functional groups carry N e.g. amines, amides, azo group, nitriles), oxygen (functional groups carry O e.g. carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (functional groups carry S e.g. thiols, thiocarbamates, thioethers). Different chelating agents can bind with metal ions with different stability. It can explain by Hard Soft Acid Base (HSAB) principle [29, 30] (sometimes called Pearson’s Principle). HSAB is the important rule which describes the stability of metal-ligand complex based on the statement that “hard acids form strongly to hard bases and soft acids form strongly to soft bases”. The coordination of complex is affected by characteristic of metal ion and chelating agents as well as conditions of sample solution (e.g. pH, ionic strength).

Ion exchange

Ion exchange is a sorptive process which used sorbent carrying positive or negative charges and the surface associated with the opposite charge as counter-ions. Counter ions are the sites that exchange with analyte ions. The sorbent which contains cationic counter ion is labeled as cation exchange. On the other hand, the sorbent which contains anionic counter ion is labeled as anion exchange.

There are two types of ion exchange: strong and weak, depends on the characteristic of functional group. Strong ion exchange is the sorbent carrying functional group which presents active form in the wide range of pH. Functional group of weak ion exchange presents active form at pH close to pK_a. The sorption efficiency is affected by analyte ions properties, ionic strength, and pH.

Ion-pairing

Ion-pairing is developed for improving retention between polar analyte and non polar sorbent by adding ion pairing agent. Ion pairing agent contains both hydrophobic and hydrophilic sites on the molecule. The sorbent is coated with ion pairing agent by hydrophobic forces. Then, the surface of sorbent possesses ionic charges. However, ion-pairing has similar mechanism to ion exchange.

2.3 Solid sorbent in SPE

The important characteristics of the sorbent are stability in wide pH range, fast kinetics and quantitative sorption and desorption, high capacity, and reusability, Solid sorbent materials in SPE are divided into two based supports as inorganic based sorbents and organic based sorbents [26].

2.3.1 Sorbents based on inorganic support

The main materials of sorbents based on inorganic support are silica gel or other inorganic oxide. They are summarized in Figure 2.2

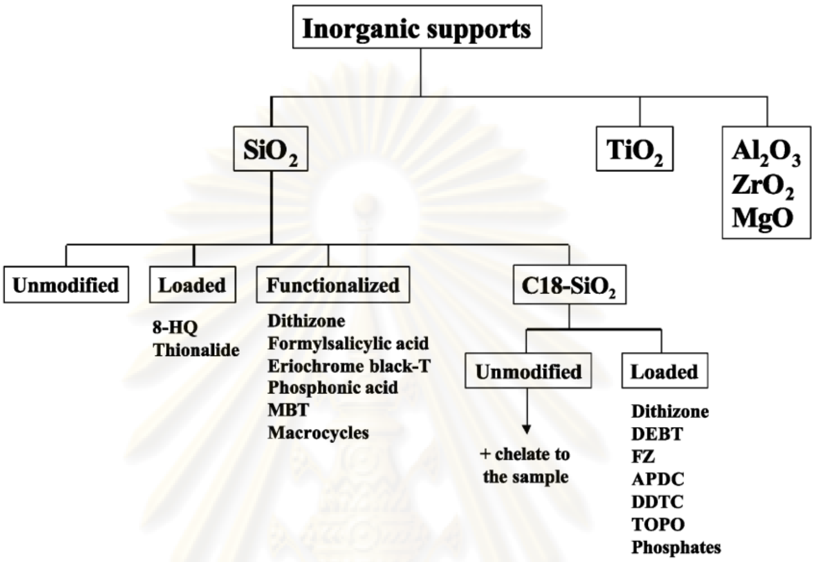


Figure 2.2 Inorganic based sorbents. [26]

Silica gel sorbent

Silica gel is basically inorganic based sorbent. It shows many advantages including not swell or strain, highly resistance to chemical and heat, high sorption capacity. Whereas, narrow pH range is the major limitation of this sorbent because the protonation of silanol group is prone at low pH.

C_{18}–bonded silica gel sorbent

Octadecyl-bonded silica gel is the common reverse stationary phase in chromatography for separation of hydrophobic sample and is not suitable for element applications. Improvement of retention for element species is successful by functionalization of C_{18}- bonded silica gel with chelating agent. In spite of silica based sorbent, C_{18}- bonded silica gel has similar drawback to silica gel.

Other inorganic oxides sorbents

Other inorganic oxides sorbents such as magnesia (MgO), titania (TiO_2), alumina (Al_2O_3), zirconia (ZrO_2), etc. have been used for retention of element species by bonding between elements and metal-O groups on the sorbent. At pH below isoelectric point, the sorbent is protonated and retains anionic species. Otherwise, cationic species are retained at pH above isoelectric point.

2.3.2 Sorbents based on organic support

Sorbents based on organic support consist of two types as polymeric and non-polymeric sorbents, depicted in Figure 2.3. The important benefit of organic sorbent over inorganic sorbent is the wide pH stability range. The retention capability of the sorbent depends on many physicochemical parameters including particle size, surface area, pore diameter, pore volume, degree of cross linking and particle size distribution. In addition, selectivity of the sorbent can be improved by modification of the sorbent with chelating ligands.

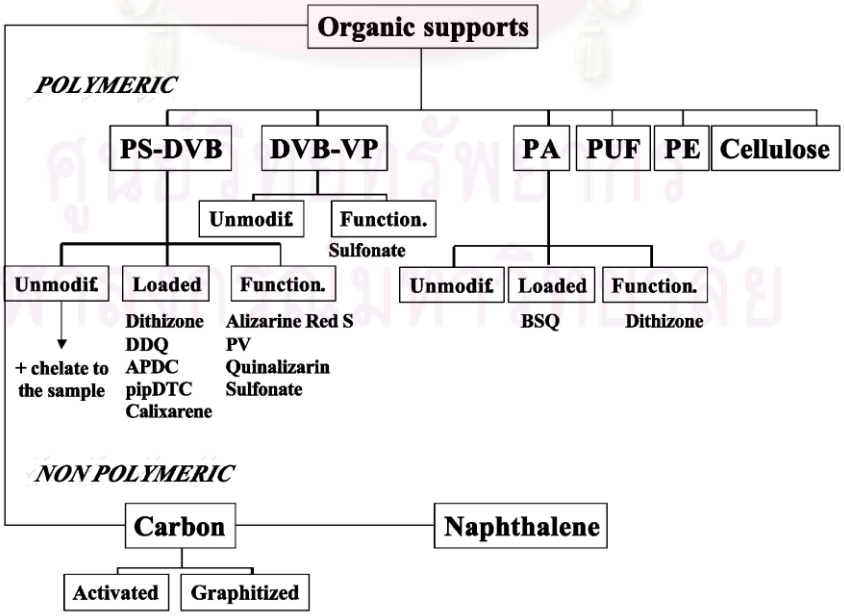


Figure 2.3 Organic based sorbents. [26]

Polystyrene-divinylbenzene sorbent

Polystyrene-divinylbenzene (PS-DVB) based sorbents are widely used. They have many aromatic rings on the surface which allow π-π interactions [31]. Chemical bonded sorbent with polar group could enhance the sorption efficiency in aqueous samples. There are many commercial PS-DVB sorbents as Amberlite XAD series such as Amberlite XAD-1, XAD-2, XAD-4, and XAD-16.

Carbon sorbent

Activated carbon sorbents can retain not only organic compounds but also elements owing to two adsorption mechanisms: Van der Waals forces or π-electron interactions, and hydrogen bonding. However, low reproducibility on account of heterogeneous active sites on the surface and its very reactive for oxidation and chemical reactions are the major drawback of this sorbents.

Cellulose sorbent

Cellulose is one of sorbents which effectively extract trace element in water sample. The selectivity becomes better by being functionalized with chelating ligands.

2.4 Lead

2.4.1 Toxicity of Pb(II)

Pb(II) which is a poisonous metal ion, can contaminate and accumulate in the environment. Many health problems occur when Pb(II) accumulates in human body. It causes the damage of brain, nervous connection, muscle, kidney, alimentary canal, gastrointestinal tract, hematological, urology, and then eventually death [2].

2.4.2 Determination of Pb(II)

The basic measurement of Pb(II) is described below.

2.4.2.1 Flame atomic absorption spectrometry (FAAS)

FAAS is the single element at a time detection method which is widely used for determination of 60-70 elements. It is suitable for routine analysis because of its merits: very simple with unskilled operator, high selectivity, reproducibility, good accuracy and precision, and less cost.

The standard methods for the determination of Pb(II) are the followings;

Direct Air-Acetylene Flame Method is proposed by the American Society for Testing and Materials (ASTM) [32], which is the applicable standard method for measurement of dissolved and total recoverable Pb(II) in water. Nevertheless, the chemical reaction in flame and high concentration of Ca^{2+} in sample solution are the main cause of inaccurate determination of Pb(II) concentration and high level of limit of detection.

Extraction/Air-Acetylene Flame Method is recommended in Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020) [33]. It used for determination of Pb(II) at the concentration level that not sufficiently high to determine by Direct Air-Acetylene Flame Method. Pb(II) can form a chelate with ammonium pyrrolidine dithiocarbamate (APDC), followed by extraction into methyl isobutyl ketone (MIBK) and aspiration into an air-acetylene flame.

FAAS has some limitations as follows high limit of detection for Direct Air-Acetylene Flame Method and more complicated for Extraction/Air-Acetylene Flame Method. Then, other techniques commonly used are described below.

2.4.2.2 Electrothermal atomic absorption spectrometry (ETAAS)

ETAAS, also known as graphite furnace atomic absorption spectrometry (GFAAS), is the discrete atomic absorption spectrometry which developed for improvement the sensitivity over FAAS. The L'vov platform is placed in the graphite to reduce sample loss and provide constant temperature environment for more reproducibility and sensitivity. Sample is dropped into a graphite tube then elements are atomized by electrical energy in four steps: desolvation, ashing, atomization, and cleaning. In general, the typical detection limit of ETAAS is 10-500 times lower than that of FAAS [34], but the instrument and consumable parts are more costly.

2.4.2.3 Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP-OES is the simultaneous multielemental emission technique which has been extensively used for element measurement. Nearly all elements are atomized by the sufficient plasma energy from argon gas. The significant characteristics of ICP-OES are long linear dynamic range, very high sensitivity, and less chemical interferences. ICP-OES can be used for many field applications such as agricultural and foods, biological and clinical, environmental and waters, and used as ionization source for mass spectrometer. However, the instrument cost and high gas consumption are the main drawback.

2.4.2.4 UV-visible spectrometry (UV-vis)

UV-vis is the commonly molecular absorption spectrometry for measurement of the absorbing ultraviolet or visible radiation molecules. It is routinely used as high-performance liquid chromatography (HPLC) and other instruments detector because of many field applications such as determination of organic, inorganic, biochemical molecules etc., high sensitivity, non-destruction of sample solution, and less operating cost. Complex of Pb(II) with various complexing agents could absorb visible radiation. Examples of complexing agents are the following [22].

Dithizone method

Dithizone (diphenylthiocarbazone) is the well-known complexing agent which used for determination of Pb(II) and other metals. It is soluble in ketones, alcohols, and chlorinated hydrocarbon solvents including carbon tetrachloride, chloroform, benzene, etc. and not stable to sunlight. The dithizone solution has green color and turn into pink solution when Pb(II)-dithizone was produced [22]. The reaction is shown in Figure 2.4.

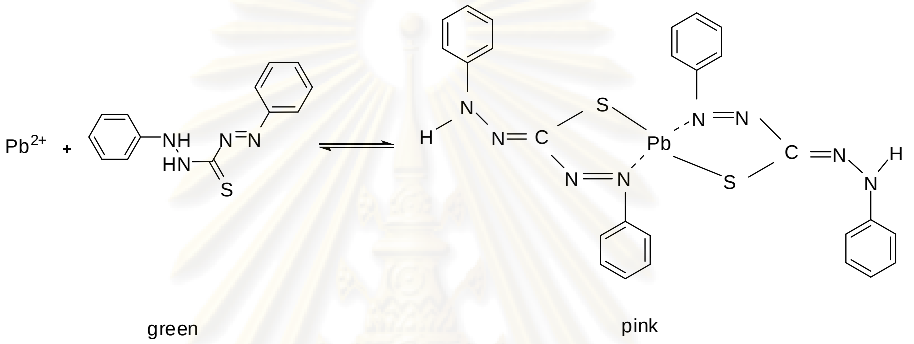


Figure 2.4 The reaction of Pb(II) and dithizone.

Pyridylazoresorcinol (PAR) method

PAR (4-(2-pyridylazo)resorcinol) is the azo compound which overcomes to dithizone owing to aqueous solution solubility. However, it is less sensitive than dithizone. Stable form of Pb(II)-PAR complex in aqueous solution has red color [22]. The structure of PAR is presented in Figure 2.5.

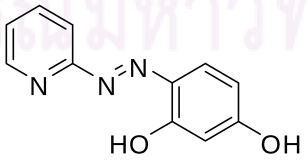


Figure 2.5 Structure of PAR.

2.5 Host-guest approach in metal-ligand complex

Host-guest chemistry is the rule which described the specific binding of substrates and macromolecule cavities through non-covalent contact including coordination bonding, ion pairing, hydrogen bonding, dipole-dipole interaction, and Van der Waals force. Host is referred to the molecule possessing convergent binding sites. And guest is referred to the molecule possessing divergent binding sites [35, 36]. Hole-size effect is the important key for the stability of complex. The complex can partially form when the rigid host cavity due to its non-flexible structure mismatches the guest molecule. If the host cavity is flexible, the stable complex can be formed owing to the changeability of the host cavity size matching to the size of guest molecule.

In many researches, selectivity of metal-ligand complex can be explained by host-guest chemistry. Examples of host molecules are crown ethers, aza macrocycles, imine macrocycles, porphyrins, calixarenes, and cyclodextrin. Frequently, a Schiff base as host molecule is widely used to bind with cationic molecule. The nitrogen atoms in many imine molecules donate electron to form complex with metal ions. The electrons delocalized across the π system, as a consequence, the metal ligand complex is stable.

2.6 Literature review

There are serious problems for determination of a heavy metal which contaminates in water. For example, the sensitivity of instruments is not enough for the quantitative analysis of trace level of metal ions and the sample has complicated matrix interference problems. Accordingly, the step of separation and preconcentration is usually required. Examples of many techniques which solved these drawbacks are the followings:

Liquid liquid extraction (LLE) is a general technique for extraction and separation of analyte from one phase into another immiscible phase. There are many metals have been extracted by using this technique [4-7]. For example, zinc hexamethylenedithiocarbamate ($Zn(HMDC)_2$) was used as extractant for the extraction of Pb(II) from other matrix elements in HNO_3 and HCl medium solutions to an organic phase containing of 2,6-dimethyl-4-heptanone (DIBK). After that, the back-extraction and determination with FAAS were approached [8].

However, solvent extraction method used large amount of organic solvent. Additionally, single drop microextraction technique (SDME) is the one technique used for reducing the use of toxic organic solvents [37-39], for instance dithizone-chloroform single drop microextraction was used for sample pre-treatment before determination of Cd(II) in water and biological samples with ETAAS. And Ir was also used as permanent modifier in a graphite tube for solving the problem of the loss of Cd(II) [40].

Nowadays, green-chemistry is a considerable concept in many fields of chemistry. For instance, room temperature ionic liquids (RTILs) have low vapor pressure, high thermal stability and can be kept away from environmental problems. With these benefits, they are interesting alternatives as nature friendly solvents [41-43]; for example, the research of Manzoori et al. [44] used 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4MIM][PF_6]$ as RTILs for preconcentration and extraction of complexes of lead ammonium pyrrolidine dithiocarbamate (Pb(II)-APDC).

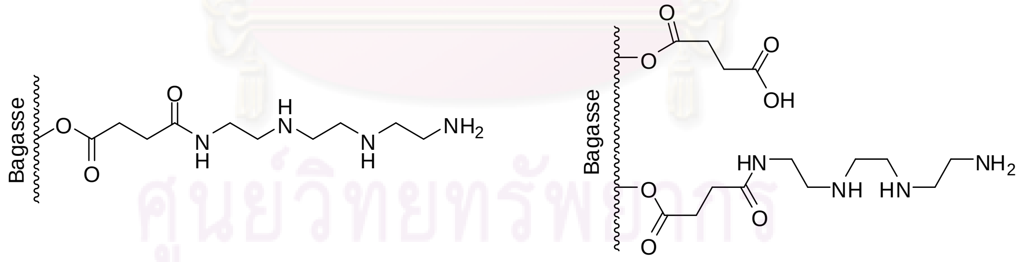
As solvent extraction has many drawbacks such as large volume of solvents, several successive extractions, emulsion between aqueous and organic phases, and necessary preconcentration step, etc., that is why, there are various methods developed for conquering these problems including ion exchange, coprecipitation, electrodeposition, membrane extraction, and solid phase extraction, etc.

The coprecipitation of Pb(II) with Co(II)-pyrrolidine dithiocarbamate complexes ($Co(PDC)_2$) prior to determination by ETAAS with slurry sampling introduction. Morewhile, ammonium pyrrolidine dithiocarbamate (APDC) was used as the chelating agent and Co(II) was used as the carrier [3]. The slurry method prosperously used for direct ETAAS determination because elution step or dissolving of the precipitate is not necessary. Anywise, the major problems that cannot be overleaped in slurry sampling method are the homogeneity and stability of the slurry. Hence, the conventional SPE is more attractive procedure than slurry method.

The most commonly used method not only preconcentration but also separation is solid phase extraction (SPE). In recent years, there are many researches on different kinds of sorbents for SPE procedure preceding determination of analytes including silica, sugarcane bagasse, activated carbon, nano-alumina etc. Examples of the researches which used various sorbents such as silica, sugarcane bagasse, activated carbon, nano-alumina, polystyrene-divinylbenzene are detailed hereafter.

Silica sorbent was modified with quaternary ammonium salt applied as matrix for the grafting of xylenol orange (XO). Thereupon, silica surface were coated with XO and Fe(III)-XO complexes as sorbent for extraction and preconcentration of Pb(II) in natural water and foodstuffs prior to determination by diffuse reflectance spectroscopy studied by Zaporozhets et al. [13].

Gurgel and Gil [14] prepared two new chelating materials based on sugarcane bagasse before functionalization with triethylenetetramine, MMSCB 3 and 5, for removal of Cu(II), Cd(II) and Pb(II) from aqueous single metal solution. The structures of MMSCB 3 and 5 are shown in Figure 2.6.



MMSCB 3

MMSCB 5

Figure 2.6 Structures of MMSCB 3 and MMSCB 5.

The surface of activated carbon was modified with tetrabutyl ammonium iodide and sodium diethyl dithiocarbamate as sorbents for elimination of Cu(II), Zn(II), Cr(VI) and CN^- from waste-water reported by Monser and Adhoum [15]. Then, activated carbon was purified and oxidized before modifying with triethylenetetramine as sorbent for preconcentration of Cr(III), Fe(III) and Pb(II) in water sample prior to determination with ICP-OES presented by Zhang et al. [16].

Ezoddin et al. [17] obtained a new effective sorbent, by coating nano-alumina with sodium dodecyl sulfate-1-(2-pyridylazo)-2-naphthol (SDS-PAN), for determination of Cd(II) and Pb(II) in water and herbs.

Furthermore the examples above, functionalization of polystyrene-divinylbenzene with various chelating agents have been widely used as polymeric sorbent in SPE method.

Mesquita et al. [18] developed a flow system for colorimetric determination of Pb(II) in water by formation of ternary complexes between malachite green, iodide and Pb(II). Anywise, this reaction was more sensitive with Cd(II) than Pb(II). Thereby, the elimination of Cd(II) was necessary. This research used AG1 X-8 as anionic sorbent for the removal of Cd(II) by complexation with chloride and retained in the sorbent. Subsequently, the mixture of sample and reagents was carried out to Chelex 100, as cationic sorbent which was combined with sequential injection for the sensitivity improvement.

Lemos and Baliza [19] developed an on-line system by functionalization of Amberlite XAD 2 with 2-aminothiophenol for preconcentration of Cd(II) and Cu(II) in water samples

In addition, Amberlite XAD-2 was coupled to purpurin for the extraction of Cd(II), Cr(III) and Pb(II) from leachate of cement-based stabilized waste and de-ionized water matrices reported by Wongkaew et al. [20]. This research showed the elimination of interferences in the samples by using SPE method.

Nutthanara et al. [21] functionalized triethylenetetamine onto polystyrene-divinylbenzene (TETA-PS-DVB) as selective sorbent for the adsorption of Pb(II), Zn(II), NI(II), Cu(II), Co(II) and Cr(III) in aqueous solution. The result showed that TETA-PS-DVB is selective for Pb(II) adsorption. The structure of TETA-PS-DVB is shown in Figure 2.7.

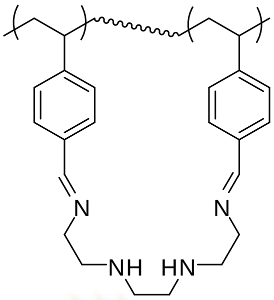


Figure 2.7 Structures of TETA-PS-DVB.

Furthermore, many literatures reported the use of dithizone as colorimetric chelating reagent for determination of heavy metal including Pb(II), Zn(II), Cd(II), Cu(II), etc. For example, Zaporozhets et al. [45] modified silica surface with dithizone and zinc dithizone as sorbent for the extraction of Ag(I), Hg(II), and Pb(II) in water and buttermilk. Many metal-dithizone forms colored chelate complexes were determined with UV-vis.

Modified alumina loaded-dithizone was used as sorbent for the removal and preconcentration of Pb(II) and other metals from water samples, reported by Mahmoud et al. [46].

However, several colorimetric chelating agents for determination of heavy metal were dissolved in organic solvent. So, LLE is always used and on account of the limitation of solvent extraction method. A new methodology by using aqueous medium containing surfactant for avoidance of organic solvent use is also attractive.

Paradkar et al. [47] used dithizone in aqueous medium containing Triton X-100 for extraction of several heavy metals. Akl [48] using phenanthraquinone monophenyl thiosemicarbazone (PPT) combined with nonionic surfactant for colorimetric determination of Pb(II) in aqueous solution.

From the literature review mentioned above, polystyrene-divinylbenzene copolymer functionalized with triethylenetetramine (TETA-PS-DVB) is the attractive sorbent for extraction of Pb(II) due to its selectivity and combination of micellar colorimetric method and desorption step is the interesting technique for determination of Pb(II) by UV-vis. This research aimed to extraction of Pb(II) in water by using TETA-PS-DVB for determination by UV-visible and flame atomic absorption spectrometries.

CHAPTER III

EXPERIMENTAL

3.1 Apparatus

Attenuated total reflectance Fourier transform infrared spectrometer

An attenuated total reflectance Fourier transform infrared spectrometer model Nicolet 6700 was used for functional group characterization of all products for each sorbent preparation step in the range of 400-4000 cm^{-1} using ATR technique.

Flame atomic absorption spectrometer

The amount of Pb(II) in solutions was determined by a flame atomic absorption spectrometer model AAnalyst 100 from Perkin-Elmer. The lead hollow cathode lamp was operated using default conditions under the recommendation of the manufacturer. The analytical wavelength was set at 283.3 nm with 0.7 nm of slit width and 10 mA of lamp current. The acetylene flow rate was controlled at 2 mL min^{-1} and the air flow rate at 4 mL min^{-1}.

Inductively coupled plasma optical emission spectrometer

An inductively coupled plasma optical emission spectrometer model iCAP 6500 duo from Thermo Scientific was used for the determination of metal ions in solutions.

Mechanical shaker

A mechanical shaker model HS 500 from Janke&Kunkel was used for shaking the solution in batch method.

Overhead mixer

An overhead mixer model Rotax 6.8 was used for the preparation of leachate solution.

Peristatic pump

The flow rates of all column method experiments were controlled by a peristaltic pump model ISM827 from ISMATEC.

pH meter

A pH meter model 744 from Metrohm supplied with a glass-combined electrode was used for the measurement of pH values of solution.

UV-visible spectrophotometer

A UV-visible spectrophotometer model HP 8453 was used for absorbance measurement of Pb(II)-dithizone complex in solution in the range of 300 and 700 nm.

3.2 Chemicals

All chemicals were used in this experiment without further purification unless otherwise noted. The chemicals were summarized in Table 3.1.

Table 3.1 Chemicals list

Chemicals	Supplier
Acid solutions (Acetic acid, Hydrochloric acid 37%, Nitric acid 65%, Sulfuric acid 98%)	Merck
Acetone	Fisher Scientific
Benzene	Merck
Chloromethylated styrene/divinylbenzene copolymers	Aldrich
Dichloromethane*	Carlo Erba Reagent/ ACS
Dimethyl sulfoxide (DMSO)	Merck/ for synthesis
1,4-Dioxane	Carlo Erba Reagent/ ACS
Dithizone	May&Baker
Ethanol	Merck
Methanol	Merck
Ninhydrin	Merck
Potassium hydroxide	Merck
Sodium acetate	Carlo Erba Reagent/ ACS
Sodium hydrogen carbonate	Merck
Stock standard solutions of Co(II), Cr(III), Cu(II), Ni(II), Pb(II), and Zn(II)	Merck
Triethylenetetramine	Fluka/ purum ≥97% (RT)
Triton X-100	Fluka

* The elimination of moisture in dichloromethane was done by distillation over calcium hydride and distilled again before used in functionalization of CHO-PS-DVB step.

3.3 Preparation of solutions

Working metal solutions

Working metal solutions of Pb(II), Zn(II), Ni(II), Cu(II), Cr(II), and Cr(III) were prepared by stepwise dilution of 1000 mg L^{-1} stock standard solution to the required concentrations by using deionized water. The pH of all solutions was adjusted by 1% (v/v) nitric acid and 1% (w/v) potassium hydroxide solutions.

Acetate buffer

The appropriate amount of CH_3COONa was dissolved in deionized water and its pH was adjusted by acetic acid solution to pH 5.5.

Hydrochloric acid solution

The HCl solutions (1, 5, 10% (v/v)) were prepared daily by direct dilution from the concentrated acid solution.

Nitric acid solution

The HNO_3 solutions (1, 5, 10% (v/v)) were prepared daily by direct dilution from the concentrated acid solution.

Potassium hydroxide solution

The 1% (w/v) KOH solution was prepared by dissolving the appropriate amount of KOH in deionized water.

Dithizone in Triton X-100 solutions

Triton X-100 solutions with the concentrations of 3, 5, and 10% (v/v) were initially prepared by dissolving the surfactant in acetate buffer. An excessive amount of dithizone powder was then added into the Triton X-100 solutions. The mixtures were continuously stirred until the saturated solutions of dithizone were obtained. Afterwards, the excess undissolved dithizone solid was separated from the solutions by means of filtration using filter paper. These solutions were daily prepared.

3.4 Preparation and characterization of sorbent

There are two main steps for the preparation of TETA-PS-DVB. The procedure was modified from Nutthanara et al. [21]. The sorbent was firstly prepared by oxidizing of chloromethylated polystyrene-divinylbenzene copolymers (5 g of Cl-PS-DVB) with approximate 2.1 g of sodium hydrogen carbonate in 40 mL of dimethyl sulfoxide (DMSO) in a round bottom flask, the mixture was stirred and refluxed at 155 °C for 6 hours on a sand bath. Afterwards, the sorbent was filtered out and washed with DMSO, hot water and dioxane:water (2:1). And the sorbent was rinsed with dioxane, acetone, methanol, dichloromethane, and benzene. The sorbent was then dried under vacuum at 100 °C and kept in a desiccator. The product was called aldehydic polystyrene-divinylbenzene (CHO-PS-DVB).

The next step was the functionalization of CHO-PS-DVB with triethylenetetramine (TETA), CHO-PS-DVB (1 g) was swollen in 10 mL of dichloromethane for 1 hour in a two-necked round bottom flask. Then, 2.64 mmol of TETA in 30 mL dicholoromethane was slowly added dropwise over a period of 30-45 minutes. And the mixture was stirred for 6 hours under nitrogen atmosphere until complete reaction at room temperature. Then, the sorbent was filtered out and washed with methanol and dichloromethane prior to vacuum dry at room temperature and kept in a desiccator, the product was labeled as TETA-PS-DVB. The products of each step were characterized with attenuated total reflectance Fourier transforms infrared spectrometry (ATR-FTIR) and ninhydrin test. The preparation procedure was presented in Figure 3.1.

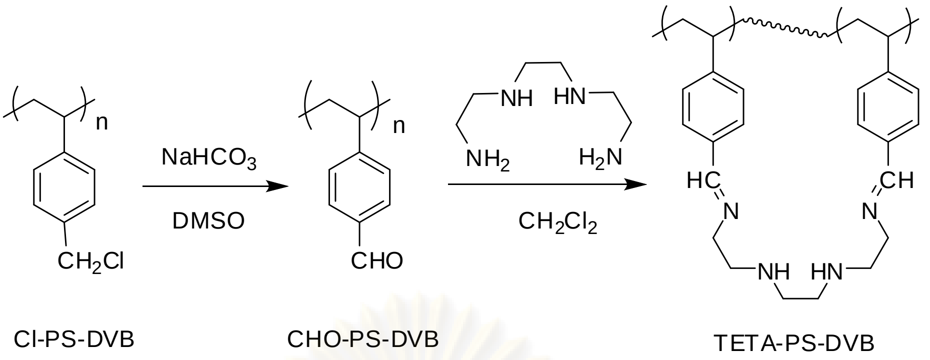


Figure 3.1 Preparation procedure of sorbent.

3.5 Preparation of leachate

Leachate from cement-based stabilized waste was prepared by following Wongkaew et al. [20] adapted from EPA method 1312 (SPLP) [49]. The cement-based mortar was ground to particle size less than 9.5 mm before extraction with extraction fluid. Since simulate natural precipitation extraction fluid was slightly acidified de-ionized water, a mixture solution of H_2SO_4:HNO_3 (80:20 by weight) was used to execute pH of deionized water to pH 5 for extraction fluid. Then, ground cement-based mortar (25 g) was leached by using 500 mL of the extraction fluid. The mixture was mixed by using an overhead mixer at 30 rpm for 18 hours. The leachate was filtered out through 0.45 µm membrane filter and preserved for further method validation experiments.

3.6 Adsorption of Pb(II) on the sorbent

The adsorptive properties of Pb(II) on the sorbent were studied in batch and column methods. All adsorption studies were investigated under optimum pH values previously reported by Nutthanara et al. [21]. All experiments were performed in triplicate.

3.6.1 Batch method

In batch method, the effect of numerous analytical parameters including sorption time, and kinetics of Pb(II) sorption, selectivity of sorbent, sorbent capacity and adsorption isotherm was investigated.

3.6.1.1 Effect of sorption time and kinetics of Pb(II) sorption

For estimating the optimum sorption time and kinetics of Pb(II) on the sorbent, the batch method was carried out by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} Pb(II) solution after being adjusted its pH to 4. Then, the screw capped test tubes was mechanically shaken at sorption times ranging from 0-120 minutes. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes. The remained amount of Pb(II) in the solution was determined by FAAS.

3.6.1.2 Selectivity of sorbent

In order to assess the selectivity of the sorbent for sorption of Pb(II), 25 mg of sorbent was weighed in screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} single Pb(II) solution pH 4 or binary solution of Pb(II) with other metals *i.e.* Zn(II), Ni(II), Cu(II), Co(II) or Cr(III) and the mixture was mechanically shaken at an optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes. The remained amount of Pb(II) in the solution was determined by FAAS.

3.6.1.3 Sorption capacity and adsorption isotherm

The sorption capacity of sorbent and adsorption isotherm were investigated by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of various concentrations of Pb(II) solution between 3.00 and 6.50 mg L^{-1} after being adjusted its pH to 4 and the mixture was mechanically shaken at an optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes. The remained amount of Pb(II) in the solution was determined by FAAS.

3.6.2 Column method

A Curity® stomach tube (0.4 cm internal diameter, 2.5 cm length) was used for preparation of a laboratory-made mini-column. Each column was packed with 50 mg of sorbent and sealed with cotton at both ends. The mini-columns were used only one time. In column method, the effect of flow rate and recirculation of solution was performed.

3.6.2.1 Effect of flow rate

The effect of flow rate was studied by passing a 25 mL aliquot of 1 mg L^{-1} Pb(II) solution through the column over a flow rate ranging of 0.5-5.0 mL min^{-1}. The flow rate of solution was controlled by a peristaltic pump. The remaining Pb(II) in the solution was determined by FAAS.

3.6.2.2 Recirculation of solution

The recirculation of solution was evaluated for improvement of the sorption efficiency. A 25 mL aliquot of 1 mg L^{-1} Pb(II) solution was passed through the column at a suitable flow rate. The remaining solution was recirculated by passing through the same column again and again at the same flow rate. The recirculation of solution was varied in the range of 2-7 cycles. The remaining Pb(II) in the solution was determined by FAAS.

3.7 Desorption of Pb(II)

For the desorption study of Pb(II) from the sorbent, the determination of Pb(II) was divided into two techniques, *i.e.* flame atomic absorption spectrometry and UV-visible spectrometry. Both FAAS and UV-vis were only evaluated in batch method.

3.7.1 Determination by FAAS

3.7.1.1 Effect of type and concentration of desorption solutions

The study of type and concentration of desorption solutions, a batch method was carried out by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} Pb(II) solution pH 4 before mechanically shaking at optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes and washed with deionized water twice, and then HNO_3 or HCl solution with different concentrations was added and shaken for 1 hour. The amount of Pb(II) in the solution was determined by FAAS.

3.7.1.2 Effect of desorption time

In order to examine the suitable desorption time, a batch method was carried out by weighing 25 mg of sorbent in the screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} Pb(II) solution (pH 4) before mechanically shaking at optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes and washed with deionized water twice, and then the suitable desorption solution was added and shaken at desorption times in a range of 0-60 minutes. The amount of Pb(II) in the solution was determined by FAAS.

3.7.2 Determination by UV-vis

For UV-visible technique, the amount of Pb(II) was determined by using saturated dithizone in surfactant solution as colorimetric chelating reagent. The color of dithizone solution changed from green to pink when Pb(II)-dithizone was produced. The absorbance of Pb(II)-dithizone complex was measurement at 515 nm.

3.7.2.1 Effect of concentration of surfactant

Dithizone is an organic colorimetric chelating agent that could not dissolved in aqueous medium. Then, a surfactant (Triton X-100) was used for enhancing solubility of dithizone in aqueous medium. This research used saturated dithizone for assuring that adequate amounts of dithizone for the amount of Pb(II) which stripped from the sorbent. However, amounts of dithizone that dissolved in aqueous solution containing surfactant depend on the concentration of surfactant; therefore, the effect of concentration of surfactant was first evaluated.

The effect of concentration of surfactant was performed by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} Pb(II) solution pH 4 and the mixture was mechanically shaken at an optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes and washed with deionized water twice, and then different concentrations of Triton X-100 containing saturated dithizone solution (5 mL) were added. The amount of Pb(II) in the solution was determined by UV-vis.

3.8 Method validation

Leachate from cement-based stabilized waste was used for demonstration of the validity of this method. Recovery was evaluated by using spiked Pb(II) to leachate. And the precision of the method was performed as the relative standard deviation (RSD).

The method validation in batch method was carried out by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of leachate spiked with 5 mg L^{-1} Pb(II) solution (pH 4) and the extraction was done under optimal conditions. The amount of Pb(II) in the solution was determined by FAAS.

3.9 Reuse of sorbent

The reuse of sorbent was carried out by weighing 25 mg of sorbent in screw capped test tubes with a 5.00 mL aliquot of 5 mg L^{-1} Pb(II) solution pH 4 and the mixture was mechanically shaken at optimum sorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes and washed with deionized water twice, and then the desorption solution (suitable desorption solution for determination by FASS or dithizone in surfactant solution for UV-vis) was added and shaken at optimum desorption time. The sorbent was separated by centrifugation at 3000 rpm for 10 minutes and washed with deionized water twice. Afterwards, the sorbent was dried under vacuum at 100 °C. The same sorption process was repeated and the amount of Pb(II) in the solution was determined by FAAS.

CHAPTER IV

RESULTS AND DISCUSSION

The content of this chapter consists of 5 parts including the characterization of the sorbent (section 4.1), the study of adsorption of Pb(II) on the sorbent in batch and column methods (section 4.2) and the desorption study (section 4.3), the validation of the proposed extraction method (section 4.4), and the reuse of sorbent (section 4.5).

4.1 Characterization of the sorbent

The presence of TETA in the functionalized polymer was confirmed using an attenuated total reflectance Fourier transform infrared spectrometry (ATR-FTIR). ATR-FTIR spectra are shown in Figure 4.1.

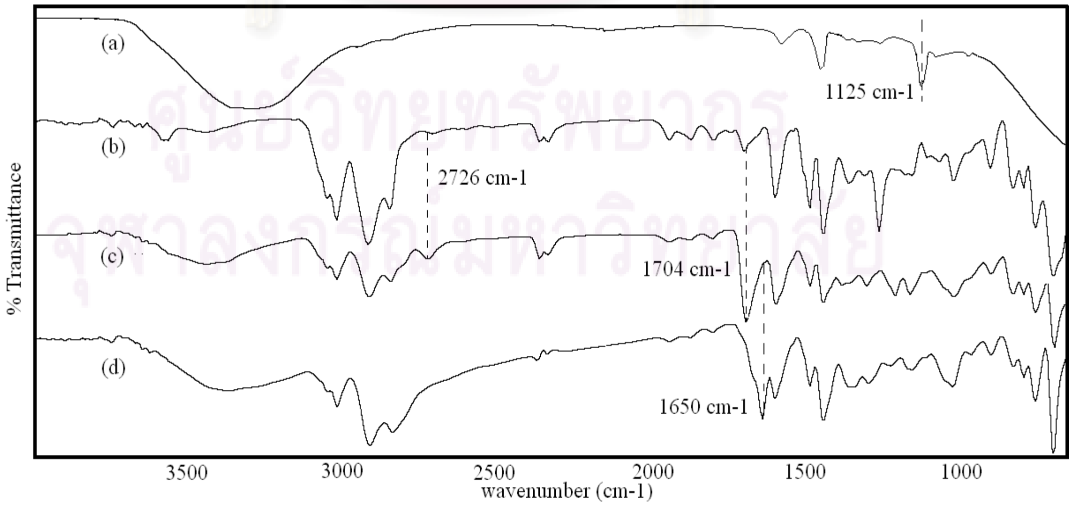


Figure 4.1 ATR-FTIR spectra of (a) TETA (b) Cl-PS-DVB (c) CHO- PS-DVB and (d) TETA- PS-DVB.

Comparing the ATR-FTIR spectra of Cl-PS-DVB with CHO-PS-DVB, CHO-PS-DVB (see the structure in Figure 3.1) showed two important characteristic peaks of aldehydric C-H stretching at 2726 cm^{-1} and C=O stretching at 1704 cm^{-1}. Moreover, comparing the ATR-FTIR spectra of CHO-PS-DVB with TETA-PS-DVB, the final product showed the presence of C=N stretching at 1650 cm^{-1} and absence of C=O stretching at 1704 cm^{-1}. Considering TETA spectrum, neither characteristic peaks of N-H nor $N\text{-}H_2$ could be observed because these peaks appear at the same wavenumber of the strong broad absorption band of water (3000-3500 cm^{-1}), but the C-N stretching at 1125 cm^{-1} could be seen. However, the C-N stretching of TETA could not be observed in the spectrum of TETA-PS-DVB.

Ninhydrin test was applied to identify whether the surface of prepared polymeric materials contained free-terminal primary amine functional group [50]. If primary amine is present, the color of the solid and solution will turn green or blue (positive test), if not, the yellow color of ninhydrin solution will not change (negative test). CHO-PS-DVB was used as a negative control while TETA was used as a positive control. The result of ninhydrin test is summarized in Table 4.1, it reveals that TETA-PS-DVB was not positive with ninhydrin. This confirmed that it did not contain any free amino group on the structure. From the IR and ninhydrin test results, the successful preparation of sorbent was assured.

Table 4.1 Results of ninhydrin test

Sample	Color of bead	Color of solution
Ninhydrin	-	yellow
TETA	-	dark blue
CHO-PS-DVB	pale yellow	yellow
TETA-PS-DVB	pale yellow	yellow

4.2 Adsorption of Pb(II) on the sorbent

4.2.1 Batch method

4.2.1.1 Effect of sorption time and kinetics of Pb(II) sorption

Sorption time is an important parameter for the attainment of equilibrium time of Pb(II) between sorbent and aqueous solution that must be investigated. Because the efficiency of Pb(II) sorption decreased when using the sorption time less than an equilibrium time for Pb(II) sorption. The mass transfer of Pb(II) in solution was enhanced using the mechanical shaker for reaching the equilibrium in a short time.

The sorption amount expressed in µmol g^{-1} resin and sorption (%) were calculated based on Equations 2 and 3, respectively.

$$sorption\ amount\,(\mu mol\ g^{-1}) = \frac{n_i - n_f}{m} \qquad (2)$$

where n_i is the initial amount of Pb(II) in the solution (µmol)

n_f is the residual amount of Pb(II) in the solution at equilibrium (µmol)

m is the amount of sorbent (g)

$$sorption\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (3)$$

where C_i is the initial concentration of Pb(II) in the solution (mol L^{-1})

C_f is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1})

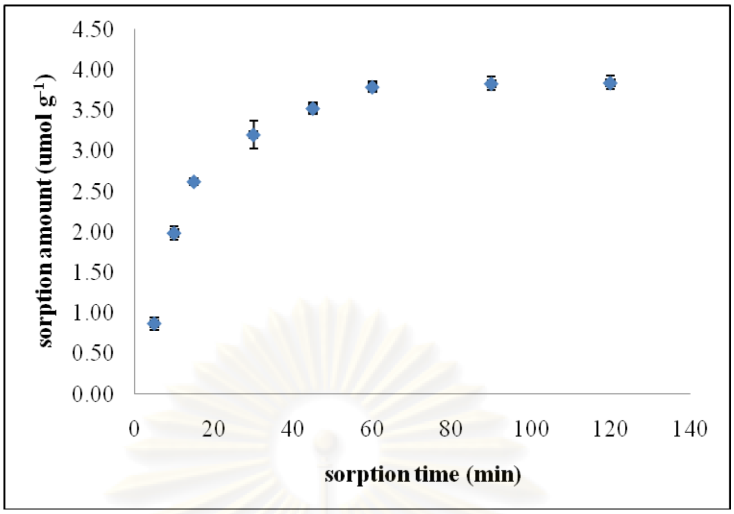


Figure 4.2 Influence of sorption time of Pb(II) on the sorbent [pH 4, 25 mg sorbent, concentration of Pb(II) = 5 mg L^{-1}, volume of Pb(II) solution = 5.00 mL (n=3)].

Figure 4.2 showed the result of the sorption amount of Pb(II) as a function of time. The sorption amount of Pb(II) was plotted versus sorption time. It is instantaneously distinguished that the sorption of Pb(II) increased rapidly at the beginning and decreased slowly until the steady state was reached. However, Pb(II) sorption was not complete in a short time. The sorption equilibrium was reached within 60 minutes with approximate 80% of Pb(II) sorption on the sorbent and increasing time after its equilibrium did not affect the quantitatively adsorbed Pb(II). Then 60 minutes was used for all subsequent experiments.

Kinetics of sorption from solution to sorbent is the considerable parameter for informative evaluation about the mechanism of sorption process. There are several adsorption kinetics models that have been established to study. The most widely used models for performing kinetics of sorption of heavy metal on many sorbents are the pseudo-first-order and pseudo-second-order rate [51-54], hence the experimental kinetics data were fitted with pseudo-first-order rate by Lagergren equation and pseudo-second-order rate for determination of the value of rate constant of Pb(II) sorption using the following Equations 4 and 5, respectively.

$$log(q_e - q_t) = log\ q_e - \frac{k_1 t}{2.303} \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where q_e is the amount of Pb(II) adsorbed per gram of sorbent at equilibrium (mol g^{-1})

q_t is the amount of Pb(II) adsorbed per gram of sorbent at any time (mol g^{-1})

k_1 is the pseudo-first-order rate constant (min^{-1})

k_2 is the pseudo-second-order rate constant (g mol^{-1} min^{-1})

t is the sorption time (min)

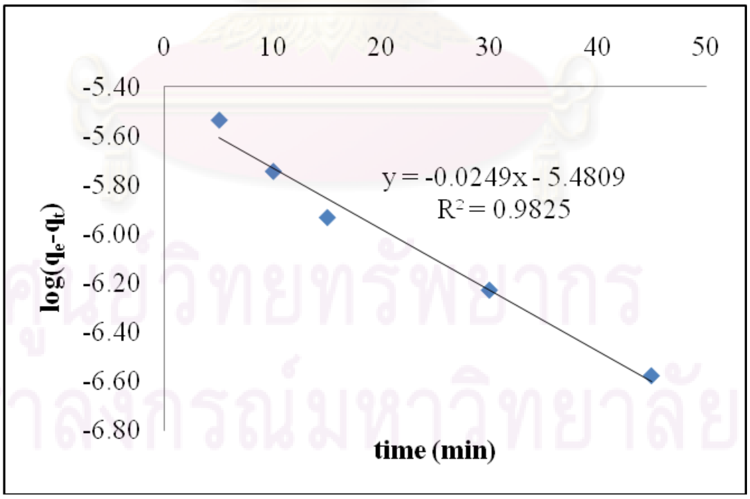


Figure 4.3 Pseudo-first-order sorption kinetics of Pb(II) on the sorbent [pH 4, 25 mg sorbent, concentration of Pb(II) = 5 mg L^{-1}, volume of Pb(II) solution = 5.00 mL (n=3)].

From Lagergren equation, $log(q_e - q_t)$ was plotted versus time. And the logarithm function was defined that the number after log must be a positive value. After equilibrium q_e is less than q_t, therefore $(q_e - q_t) \leq 0$. Then, only experimental data before equilibrium was considered.

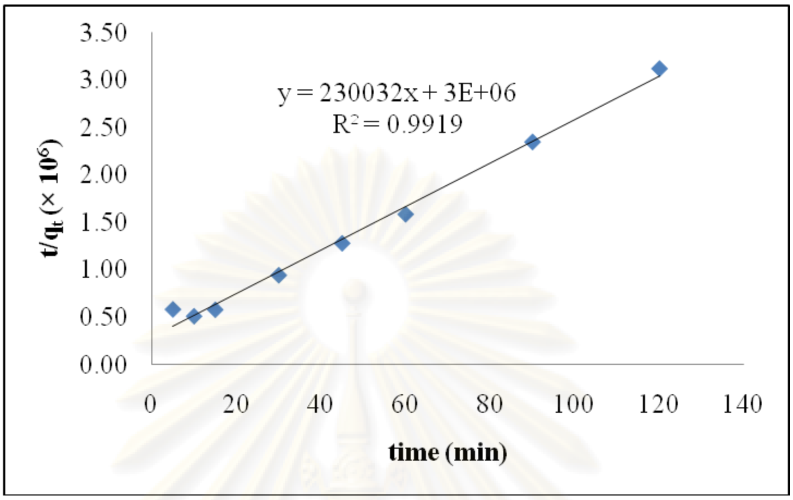


Figure 4.4 Pseudo-second-order sorption kinetics of Pb(II) on the sorbent, [pH 4, 25 mg sorbent, concentration of Pb(II) = 5 mg L^{-1}, volume of Pb(II) solution = 5.00 mL (n=3)].

Figure 4.3 and Figure 4.4 presented that both pseudo-first-order rate and pseudo-second-order rate exhibited good linearity. But this mechanism was presupposed to be chemisorption. In chemisorptions process, the rate of reaction depends on both active sites on sorbent surface and sorbate ions. Then, the pseudo-second-order model should be more suitable than the pseudo-first-order one. The pseudo-first-order result might be as a result that the sorbent has so many active sites than the amount of Pb(II) in solution. The kinetics depends on only the sorbent. Consequently, better linearity from pseudo-first-order rate ($R^2 > 0.98$) was obtained. The rate constant k_2 derived from the graph was to be 18425 g mol^{-1} min^{-1}.

4.2.1.2 Selectivity of sorbent

The selectivity of sorbent for Pb(II) adsorption in binary mixture solution was assessed, even though Nutthanara et al. [21] studied the sorption of many metal ions *i.e.* Pb(II), Co(II), Cr(II), Cu(II), Ni(II), and Zn(II) in single metal solution.

Pb(II) adsorption ability might be decreased due to the competition among metal ions in mixture solution. The result is presented in Table 4.2.

Table 4.2 Amount of Pb(II) adsorbed on the sorbent

Solution	Sorption of Pb(II) (μmol g^{-1})*	Sorption of competing ions (μmol g^{-1})*
Pb(II)	3.85 ± 0.07	-
Pb(II) / Co(II)	4.12 ± 0.12	0.00 ± 0.00
Pb(II) / Cr(III)	4.19 ± 0.06	4.10 ± 0.06
Pb(II) / Cu(II)	3.92 ± 0.06	0.70 ± 0.05
Pb(II) / Ni(II)	4.10 ± 0.00	0.00 ± 0.00
Pb(II) / Zn(II)	4.29 ± 0.07	0.10 ± 0.07

*mean±SD (n=3)

The result in Table 4.2 reveals that the same amount of Zn(II), Ni(II), Cu(II), Co(II) and Cr(III) with Pb(II) did not considerably change the adsorption ability towards Pb(II). The Pb(II) adsorpability increased slightly when the competing metal ions were present in the solution. It could be explained according to Le Chatelier’s Principle, when a dynamic equilibrium of the system was disturbed by changing the concentration, the equilibrium position will shift in the way to counteract the change. The binary mixture solutions had either higher concentration of ions. Then, the alteration of the system was neutralized by decreasing ions concentration in consequence of increasing sorption efficiency.

The strong affinity of Pb(II) could be explained by not only Hard Soft Acid Base Principle (HSAB), but also the ionic radius of the ions [35, 36]. The metal ions were categorized as Lewis acids. The metal ions and their ionic radius were demonstrated in Table 4.3.

Table 4.3 Categorization and ionic radius of the studied metal ions [55]

Ionic radius (pm)	Hard	Borderline				
	Cr(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Pb(II)
6 coordination	76	79	83	87	88	133
4 coordination	-	72	63(sq) 69	71	74	-

According to HSAB, R_2NH could be classified as borderline-soft Lewis base. Therefore, Cr(III) in single metal solution might not prefer to form complex with amine group on the sorbent as reported by Nutthanara et al. [21]. But from the experiment data, Cr(III) in binary mixture solution could be adsorbed on the sorbent. This abnormal phenomenon might be described that, at the pH 4 Cr(III) was hydrolyzed to $[Cr(OH)]^{2+}$ [29], and Cr(III) could form bimetallic complexes with amine-phenolate ligands [56] or quadridentate amines [57] using a hydroxyl group (μ-OH) as a bridge between two Cr(III) centers. From this supporting data, we proposed that a bimetallic complex based on Pb−(μ-OH)−Cr might presumably form on the sorbent surface. As a result, Cr(III) in the binary solution could be retained on the TETA-PS-DVB.

In addition to ionic radius, there are significant differences in ionic radius between Pb(II) and Co(II), Ni(II), Cu(II), and Zn(II). From the experimental result, it suggests that the cavity site of the sorbent should be suitable for the ionic radius of Pb(II).

4.2.1.3 Sorption capacity and adsorption isotherm

The sorption capacity of the sorbent for the retention and the adsorption behavior of Pb(II) on the sorbent were also investigated. The sorption capacity is the significant factor that presented many quantitative amount of metal ion adsorbed on the sorbent. The equilibrium experimental data under optimal sorption conditions were fitted with Langmuir, Freundlich, and Temkin models. The Langmuir, Freundlich, and Temkin models are described by Equations 6, 7 and 8, respectively [58-60].

$$\frac{C}{N_f} = \frac{1}{bN_s} + \frac{C}{N_s} \tag{6}$$

where C is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1})

b is the Langmuir constant related to energy of adsorption (L mol^{-1})

N_f is the amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1})

N_s is the maximum amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1})

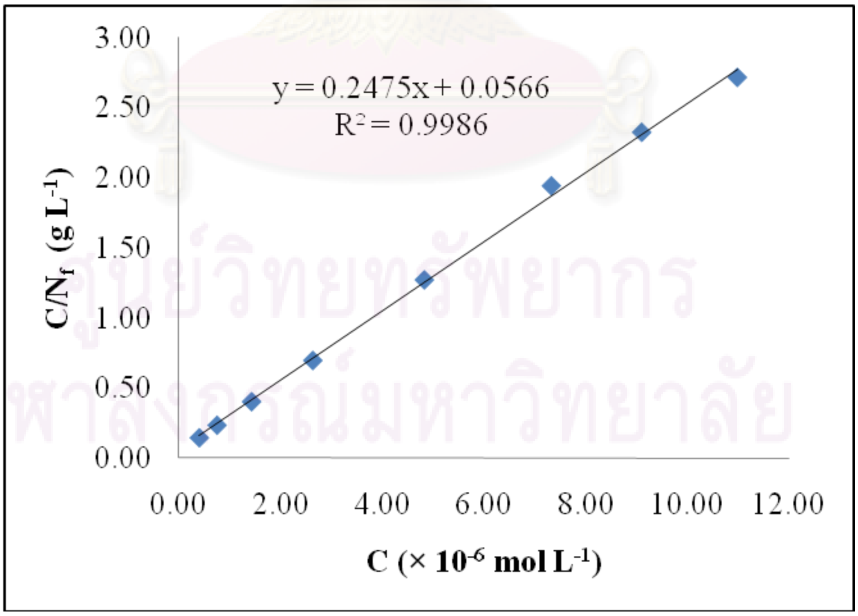


Figure 4.5 Langmuir isotherm of Pb(II) on the sorbent.

$$\log N_f = \log K - \frac{1}{n} \log C \qquad (7)$$

where	C	is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1})
	N_f	is the amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1})
	n	is the Freundlich constant related to adsorption intensity
	K	is the Freundlich constant related to adsorption capacity

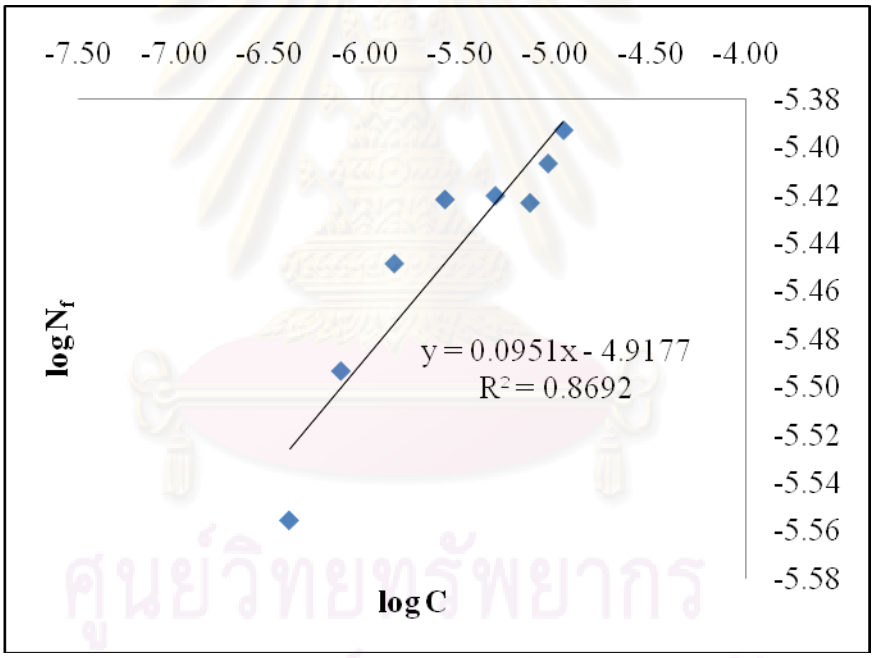


Figure 4.6 Freundlich isotherm of Pb(II) on the sorbent.

$$N_f = \frac{RT}{b} \ln K_T - \frac{RT}{b} \ln C \qquad (8)$$

where C is the residual concentration of Pb(II) in the solution at equilibrium (mol L^{-1})

N_f is the amount of Pb(II) adsorbed per gram of sorbent (mol g^{-1})

K_T is equilibrium binding

R is the gas constant (8.314 J mol^{-1})

T is the absolute temperature

b is related to the heat of adsorption

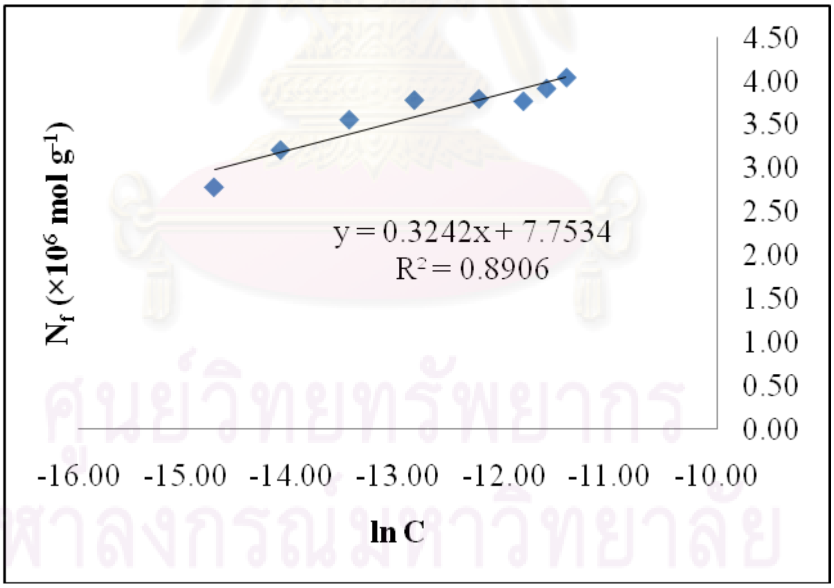


Figure 4.7 Temkin isotherm of Pb(II) on the sorbent.

Langmuir adsorption model is based on the assumption that the sorbent has homogeneous active sites on the surface. Sorbates adsorb as monolayer on the sorbent with constant energy and each binding site can occupy one metal ion. The

Langmuir constant (b) relates to the stability of sorbate-sorbent complex. The maximum capacity (N_s) can calculate from the Langmuir equation.

Freundlich adsorption model is based on the assumption that the sorbent has heterogeneous surface energy. Sorbates can occupy as multilayer on the sorbent with variations in heat of adsorption. The adsorption capacity (K) can determine from the Freundlich equation. The Freundlich constant (n) relates to adsorption intensity which indicate to the degree of favorability of adsorption.

Temkin adsorption model is based on the assumption that interaction between sorbate and sorbent as a result of linearly decreasing of the heat of adsorption. The adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The heat of adsorption (b) and maximum binding energy are considered from the Temkin equation ($K_T = exp(\frac{-\Delta G_{max}}{RT})$).

From the results in Figure 4.5, Figure 4.6 and Figure 4.7, only the regression correlation coefficient (R^2) from Langmuir adsorption isotherm was obtained more than 0.99. But the unfavorable regression correlation coefficients were presented in Freundlich and Temkin adsorption isotherms. It exposes that Pb(II) adsorption on the preparative sorbent obeyed Langmuir adsorption isotherm. It could be assumed that the surface has homogeneous active sites, Pb(II) adsorbed as monolayer on the sorbent and there are no other interactions for instance sorbent and adsorbate interactions or interaction between adsorbate on contiguous sites [61]. The calculated maximum adsorption capacity and Langmuir constant were 4.04 µmol g^{-1} and 4.37 × 10^6 L mol^{-1}, respectively. The high value of Langmuir constant signifies that Pb(II) was directly coordinated with the active site on the sorbent. The comparison of sorption capacities of TETA-PS-DVB for Pb(II) with other functionalized polystyrene-divinylbenzene sorbent was shown in Table 4.4. The sorption capacity of TETA-PS-DVB was higher than that of PS-DVB containing Alizarin Red-S and salicylic acid but lower than the others.

Table 4.4 Comparison of sorption capacities of TETA-PS-DVB for Pb(II) with other functionalized polystyrene-divinylbenzene sorbent.

Solid support	Sorption capacity of Pb(II) (umol g^{-1})
TETA (this work)	4.04
purpurin [20]	82.7
diethyldithiocarbamate [62]	31.1
o-aminobenzoic acid [63]	60.0
2-hydroxy-propiophenone-4-phenyl-3-thiosemicarbazone [64]	35.0
Alizarin Red-S [65]	1.5
salicylic acid [66]	2.2

4.2.2 Column method

In dynamic sorption process, the solution was passed through the sorbent while the analyte was continuously extracted from the sample. It has many strong points over static sorption for example, phase separation step is not needed, contact between the analyte ions and the sorbent in dynamic sorption is much better than static sorption, and the automation system is easily set [67]. Nevertheless, there are some necessary requirements for dynamic sorption. The sorption mechanism must have efficient kinetics in the short time. The sorbent must has high porosity for reducing back pressure in the system. And the sorbent must has high capacity for avoidance the breakthrough problem.

4.2.2.1 Effect of flow rate

One of the significant parameters in the dynamic sorption process is the flow rate of solution because the kinetics of mass transfer depends on the time. If too high flow rate is applied, the solution was passed through the column very fast. Thus, there is not enough time for Pb(II) sorption on the sorbent and poor capability of Pb(II) sorption may obtain. For this reason, the flow rate was optimized. The effect of flow rate was studied by passing a 25 mL aliquot of 1 mg L^{-1} Pb(II) solution through the column over flow rates ranging of 0.5-5.0 mL min^{-1} and the result was reported by sorption percentage.

Even the solution was passed through the column at the lowest flow rate at 0.5 mL min^{-1}, the efficiency of Pb(II) sorption was quantitatively very low with only 32% sorption. So it was not useful to study at higher flow rates. The flow rate at 0.5 mL min^{-1} was set for sub-experiments.

4.2.2.2 Recirculation of solution

Due to the low sorption efficiency of Pb(II) on the sorbent in the column method, the recirculation of solution was evaluated for improvement of the Pb(II) sorption [20]. One cycle means that a 25 mL aliquot of solution was passed through the column at 0.5 mL min^{-1}. The result was presented in Figure 4.8. The sorption percentage of Pb(II) was plotted versus number of cycles.

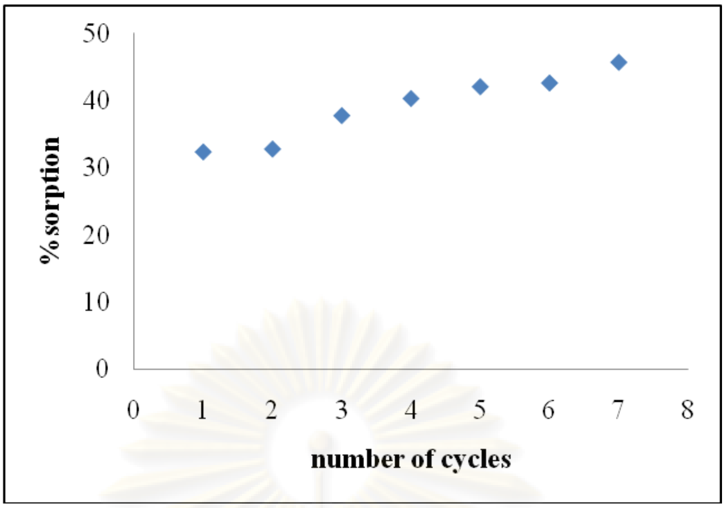


Figure 4.8 Sorption percentage of Pb(II) in column method using recirculation of solution [pH = 4, sorbent weight = 50 mg, concentration of Pb(II) = 1 mg L^{-1} sample volume = 25 mL (n=3)].

The result in Figure 4.8 illustrated visually a little increase of sorption of Pb(II). The sorption percentage depended additionally on the number of cycles. The solution was passed through the column for 7 cycles. However, the sorption efficiency was still low (<50%). The possible reason of this phenomenon was the very slow kinetics of sorption (according to the kinetics previously studied in section 4.2.1.1). The sorption did certainly not reach the equilibrium in the column (observed from Figure 4.8 that the graph did not reach a plateau). It was verified that this sorption process has very slow kinetics.

In order to explore the capability of Pb(II) sorption between the batch and column methods, the comparison of the ability of Pb(II) sorption by the two methods was performed using the same conditions such as initial concentration of Pb(II) solution, volume of the solution and sorption time. The result was given in Table 4.5. The experimental conditions were that the initial concentration of Pb(II) was 1 mg L^{-1}, the sample volume was 25 mL, the resin weight was 25 mg and the contact time was 25 hours.

By comparing the sorption percentage obtained from section 4.2.1.1 (sorption percentage ≈ 80%; using 5 mL of 5 mg L^{-1}) with the result presented in Table 4.5 (~56%; 25 mL of 1 mg L^{-1}), the former was higher. Lower sorption percentage (~56%) might be due to the fact that larger sample volume (25 mL) was used, resulting in lower possibility of sorbate-sorbent contact at the liquid-solid phase interface. Therefore, enlargement of solution volume was the main cause of poor sorption efficiency of Pb(II).

The result in Table 4.5 shows that the sorption percentage in column method was slightly higher than that of batch method, due to the fact that when the sample flowed through the packed sorbent particles in the column, the solute Pb(II) had more possibility to contact and re-contact another particles resulting in higher possibility to form complex with ligand moieties present on the sorbent surface. However, time-consuming is the main disadvantage for efficient sorption in column method. Then, this finding suggests that the sorption in column method was not recommended for subsequent experiments and future application.

Table 4.5 Comparing ability of Pb(II) sorption in batch and column methods Influence of sorption time of Pb(II) on the sorbent [pH 4, 25 mg sorbent, concentration of Pb(II) = 5 mg L^{-1}, volume of Pb(II) solution = 5.00 mL (n=3)].

Method	Sorption (%)
Batch	56.64 ± 1.59
Column	64.91 ± 0.57

4.3 Desorption of Pb(II)

4.3.1 Determination by FAAS

The amount of Pb(II) retained on the sorbent had to be stripped by appropriate desorption solution before its determination. Many parameters which affect desorption efficiency were investigated for completely eluting Pb(II) from the sorbent.

4.3.1.1 Effect of type and concentration of desorption solutions

The retention mechanism between Pb(II) and active sites on the sorbent is the major factor for contemplation of the desorption solution. TETA was functionalized on the sorbent through Schiff base at the both ends. The other amino group were act as donor atoms to coordinate with Pb(II). Then Pb(II), the retention mechanism between Pb(II) and TETA-PS-DVB is chelating mechanism. There are many researches show that acid solution such as HNO_3, HCl could be completely eluted metal from the sorbent [17, 68, 69]. Desorption efficiency expressed in desorption (%). It was calculated based on Equation 9.

$$desorption\ (\%) = \frac{n_e}{n_s} \times 100 \qquad (9)$$

where n_e is the amount of Pb(II) stripped from the sorbent (mol)

n_s is the amount of Pb(II) retained on the sorbent (mol)

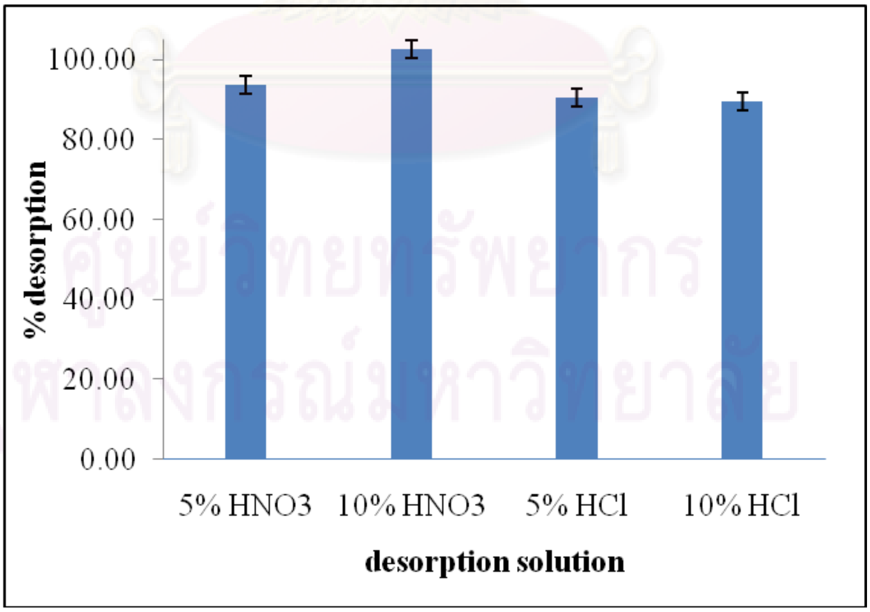


Figure 4.9 Effect of type and concentration of desorption solutions [pH = 4, sorbent weight = 25 mg, concentration of Pb(II) = 5 mg L^{-1}, volume of desorption solution = 5.00 mL (n=3)].

The effect of type and concentration of desorption solution were studied for complete elution of Pb(II) from the sorbent. The result was given in

Figure 4.9, all of the desorption solutions could desorb Pb(II) which previously retained on the sorbent. But only 10% (v/v) HNO_3 could quantitatively desorb Pb(II) with more than 95% desorption. Then 10% (v/v) HNO_3 was the most suitable desorption solution and used for method validation.

4.3.1.2 Effect of desorption time

Desorption time is an important parameter like sorption time. The equilibrium time for desorption of Pb(II) was examined using 10%(v/v) HNO_3 as desorption solution. The result of the desorption as a function of time was shown in Figure 4.10.

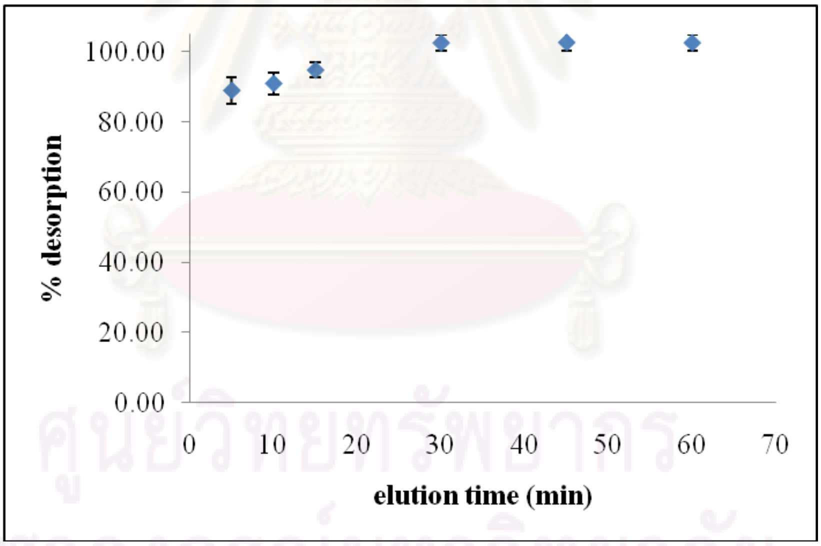


Figure 4.10 Effect of desorption time [pH = 4, sorbent weight = 25 mg, concentration of Pb(II) = 5 mg L^{-1}, volume of desorption solution = 5.00 mL (n=3)].

The desorption was plotted versus time. It is clearly observed that the desorption of Pb(II) was high at the beginning and approached rapidly the equilibrium. The desorption of 102% (or 80% recovery calculated by taking the sorption percentage of 78%) was obtained within 30 minutes and increasing time provided similar results. Then 30 minutes was used for method validation.

4.3.2 Determination by UV-vis

UV-vis is an attractive technique owing to its less operating cost and non-destruction of sample solution. Saturated dithizone in surfactant solution was used as desorption solution for stripping Pb(II) from the sorbent in the desorption step. It avoided not only using organic solvent, but also included desorption and complexing formation steps into one step.

4.3.2.1 Effect of concentration of surfactant

The UV-vis absorption spectra of Pb(II)-dithizone complex were given in Figure 4.11.

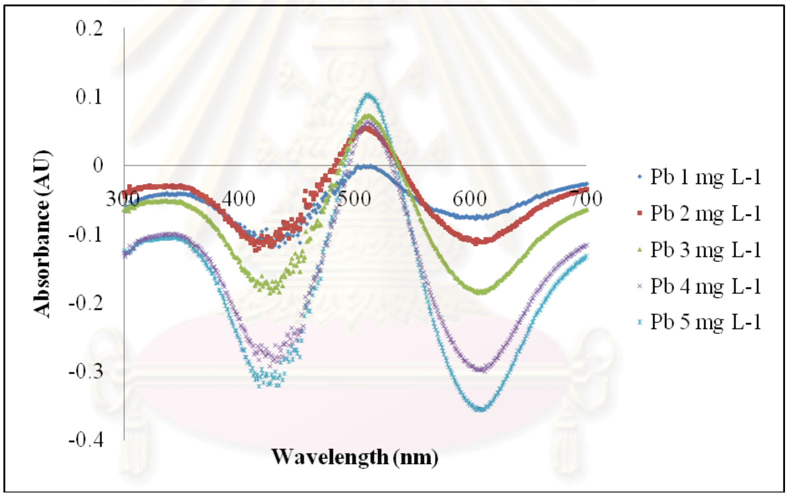


Figure 4.11 UV-visible spectra of Pb(II)-dithizone complex at various Pb(II) concentrations.

The saturated dithizone solution in acetate buffer was used as a blank for subtraction of sample spectra, based on the assumption that the difference between the amount of dithizone in Triton X-100 solution before and after elution step was negligible. A significant peak was observed in the visible region and the wavelength of the absorbance maxima at 515 nm was used for establishing a calibration curve. Background correction was done by three-point (Morton-Stubbs) correction method. The correction procedure was presented in Figure 4.12. A straight line is connected between two valley base-line of the spectrum (λ_2 and λ_3). The corrected absorbance

(A_c) is expressed by the height of the absorption peak at absorbance maxima (515 nm) that corresponds to the absorbance scale (*y*-axis) or is equal to the addition of A_1 and A_i. The calibration curve (Figure 4.13) was built by plotting A_c against concentrations of standard Pb(II) solutions.

The maxima spectra increased quantitatively with increasing the amount of complex (see Figure 4.11) which obeyed Beer–Lambert law. From the calibration curve in Figure 4.13, the correlation coefficient (R^2) was more than 0.99. It reveals that dithizone in micelle could be formed complex with Pb(II) completely. Then, this method could be used for quantitative stripping of Pb(II) before its determination by UV-visible spectrometry.

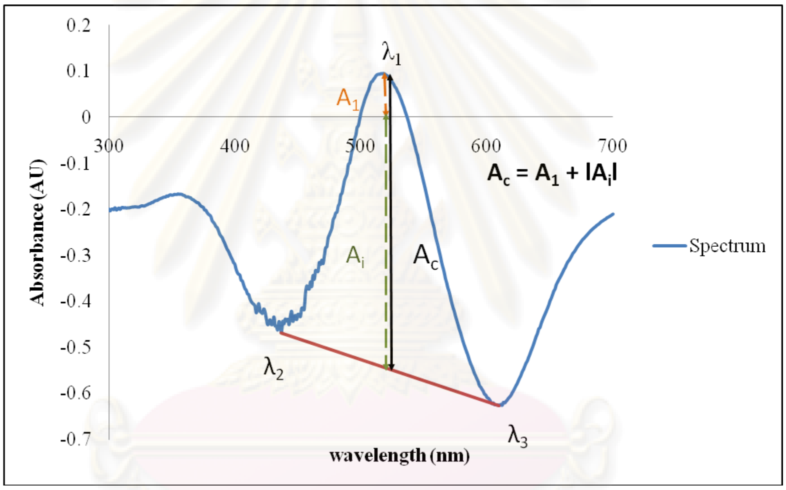


Figure 4.12 Measurement of corrected absorbance by means of three-point (Morton-Stubbs) correction.

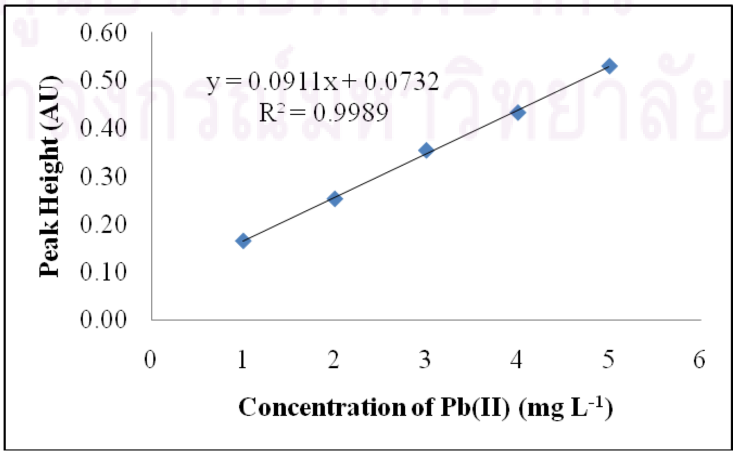


Figure 4.13 Calibration curve of Pb(II)-dithizone complex.

The effect of concentration of surfactant is illustrated in Table 4.6. The results showed that dithizone in 7% (v/v) Triton X-100 was more suitable than the others. It gave the best desorption percentage and the lowest standard deviation (SD). Higher concentration of Triton X-100 at 10% (v/v) was also evaluated for dithizone dissolution, it was found that the amount of dithizone dissolved in the surfactant solution was similar to that obtained by 7% (v/v) Triton X-100 (data not shown).

Higher concentration of Triton X-100 enhanced the solubility of dithizone. Then, the least solubility of dithizone was acquired in 3% (v/v) Triton X-100 (Table 4.6). The desorption percentage (~118%) using dithizone in 3% (v/v) Triton X-100 that was much more than 100%, might due to the largest difference in blank absorbance and Pb(II)-dithizone absorbance. The higher the concentration of Triton X-100, the closer to 100% the desorption percentage. Thus, dithizone in 7% (v/v) Triton X-100 in acetate buffer (pH 5.5) was a suitable eluent for Pb(II) desorption and UV-vis determination.

Table 4.6 Effect of Triton X-100 concentration for stripping of Pb(II) from the sorbent [pH 4, 25 mg sorbent, concentration 5 mg L^{-1} Pb(II) (n=3)]

Concentration of Triton X-100, % (v/v)	Ratio of dissolved dithizone and Pb(II)	Desorption (%)*	Recovery (%)*
3	22.82	118.86 ± 4.79	86.40 ± 1.86
5	29.45	114.90 ± 3.35	85.62 ± 0.99
7	34.68	103.73 ± 2.29	84.44 ± 0.51

*mean±SD (n=3)

4.4 Method validation

We attempted to demonstrate the performance of TETA-PS-DVB for extraction of Pb(II) from high matrix aqueous sample. Leachate from cement-based stabilized waste was selected as model aqueous sample due to high concentration of metal ions (see Table 4.7) The validity of this method was investigated using leachate from cement-based stabilized waste spiked with Pb(II). The validation results were expressed in terms of recovery and RSD for both FAAS and UV-vis determination. Recovery (%) was calculated based on Equation 10. The recoveries of the extraction of Pb(II) in the leachate sample and their RSD were given in Table 4.8.

$$re\,cov\,ery\ (\%) = \frac{n_f}{n_i} \times 100 \qquad (10)$$

where n_i is the initial amount of Pb(II) in the solution (mg)

n_f is the amount of Pb (II) stripped from the sorbent (mg)

Table 4.7 Concentration of interfering ions from semi-quantitative analysis by ICP-OES

Solution	Concentration of interfering ions (mg L^{-1})			
	Ca^{2+}	K^+	Na^+	Mg^{2+}
Leachate sample	671	529	179	27
Extracted leachate sample	3	0.8	9	0.6

Table 4.8 Recovery of Pb(II) in the leachate sample.

Sorbent (mg)	FAAS		UV-vis	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
25	65.43	3.27	65.67	3.37
50	79.01	2.71	79.59	2.71
75	82.29	2.19	83.42	2.58

The capability of Pb(II) sorption onto 25 mg of TETA-PS-DVB was significantly different in two mediums (deionized water in section 4.2.1 and leachate). That meant that high concentration of main interfering ions in the leachate *i.e.* Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+} affected the capability of the sorbent.

The result in Table 4.8 showed that increasing the dose of sorbent could improve the recovery of Pb(II). 75 mg of sorbent was adequate for extraction of Pb(II) due to satisfactory criteria for accuracy (% recovery) and precision (% RSD) [70] for both FAAS and UV-vis determination. Increasing sorbent dose may possibly increase the recovery.

The blank extraction was done using the similar conditions (which were 25 mg of sorbent, 1 hour extraction time and 10% (v/v) HNO_3 as eluent and 30 minute desorption) in order to evaluate the effect of interfering ions that might interfere or be extracted by TETA-PS-DVB. The concentration of the interfering ions presented in the desorption solution was determined by ICP-OES. The result is shown in Table 4.7. It was seen that the interfering ions were not removed from the leachate by the extraction using TETA-PS-DVB. The separation of Pb(II) from their matrices has significant advantage to extend the use of the instrument and low maintenance cost. Because matrices may cause clogging in nebulizing or tubing systems or contamination in atomizer, the sample should be cleaned up before determination. Moreover, some element matrices which form thermally stable oxide are reason of burner contamination and clogging. And they might cause unstable flow rate of fuel and oxidant gas resulting in fluctuation in measuring signals.

4.5 Reuse of sorbent

The reusability of the sorbent after being used for Pb(II) desorption by FAAS and UV-vis determination was investigated. The ability of Pb(II) sorption decreased to 2 and 63% for its determination by FAAS and UV-vis, respectively. The decline of sorption efficiency suggests that the active sites of the sorbent might probably be destroyed by the desorption solution. These propose that in case of 10% (v/v) HNO_3 used in FAAS determination, this severe desorption solution might break the imine bonds (C=N) between TETA and PS-DVB. For saturated dithizone in Triton X-100 desorption solution used in UV-vis determination, Pb(II) could be eluted by dithizone solution according to the high value of formation constant of Pb(II)-dithizone complex. The binding site of ligand might not be interrupted in mild condition. Additionally, nitrogen atoms on TETA-PS-DVB might be protonated in presence of acetate buffer (pH 5.5). Therefore some of the active sites were changed to inactive, resulting in decrease of second sorption process. Therefore, the sorbent could be used only once.

CHAPTER V

CONCLUSION

In sorbent preparation step, Cl-PS-DVB sorbent was oxidized with sodium hydrogen carbonate in DMSO. The pale yellow bead was obtained and labeled as CHO-PS-DVB. Afterwards, CHO-PS-DVB was chemically bonded with TETA and the product was called TETA-PS-DVB. ATR-FTIR analysis suggested that the expected products were successfully prepared. The products of each step were not positive with ninhydrin test indicating that no free primary amine was presented on the TETA-PS-DVB surface.

The optimal conditions have been studied in batch and column methods. In batch method, the sorption of Pb(II) reached steady state within 60 minutes with approximate extraction percentage of 80%. The kinetics of sorption fitted pseudo-first-order model and pseudo-second-order model. However, the proposed sorption process pointed to that the pseudo-second-order was more suitable than the pseudo-first-order. It was found that the preparative sorbent provided high selectivity for Pb(II) extraction. Under optimal conditions in batch method, the equilibrium experimental data were fitted with the isotherm of Langmuir, Freundlich, and Temkin models. Only Langmuir adsorption isotherm exhibited a good linearity. The maximum sorption capacity and Langmuir constant corresponded with a value of 4.04 μmol g^{-1} and 4.37×10^6 L mol^{-1}, respectively. The sorption capacity is higher than some PS-DVB-based sorbents [65, 66].

In column method, although the solution was passed through the column at the lowest flow rate, it was not efficient enough of Pb(II) sorption. Then, the recirculation of solution was carried out for improvement of the Pb(II) sorption. However, the sorption did certainly not reach equilibrium hence the sorption in column method was not recommended for the adsorption, desorption and method validation experiments.

The desorption study in batch method and Pb(II) determination step was divided into two techniques, *i.e.* FAAS and UV-vis. For the determination by FAAS, 10% (v/v) HNO_3 was the suitable desorption solution which stripped Pb(II) with more than 95% desorption within 30 minutes. And for the determination by UV-vis, the saturated dithizone in 7% (v/v) Triton X-100 solution was an appropriate desorption solution which stripped Pb(II) nearly 100% desorption.

The method validation showed good accuracy (82.29 and 83.42 % recovery for determination by FAAS and UV-vis, respectively) and good precision (2.19 and 2.58 % RSD for determination by FAAS and UV-vis, respectively) which meet satisfactory criteria.

Suggestions for future work

1. To confirm the hypothesis of the retention of Cr(III) on the sorbent in presence of Pb(II), the selectivity study should be done by varying the ratio of Pb(II) and Cr(III) in binary mixture solution or changing interfering ion which is hard acid and can be hydrolyzed and formed hydrogen bonding with Pb(II) on the sorbent.
2. To enhance the sorption efficiency, the effect of anion interference should be investigated.
3. To develop this method, the effect of sorbent dose should be performed for preconcentration of Pb(II).
4. This method should be applied for other waste samples.

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