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REMOVAL OF INORGANIC ARSENIC FROM WATER USING IRON(III)-
LOADED ZEIN BASED ADSORBENT

Miss Sineephan Thanawatpootawee



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

Faculty of Science

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สินีพรรณ ธนวัฒน์พูนทวี : การขจัดอาร์เซนิกอนินทรีย์จากน้ำด้วยตัวดูดซับฐานซิงค์เสริมเหล็ก (III) (REMOVAL OF INORGANIC ARSENIC FROM WATER USING IRON(III)-LOADED ZEIN BASED ADSORBENT) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.ณรงค์ ประไพรัชสิทธิ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร.อภิชาติ อิมยิ้ม, 70 หน้า.

โปรตีนซิงค์เป็นผลพลอยได้จากอุตสาหกรรมทางการเกษตร ถูกนำมาดัดแปรร่วมกับสารประกอบเหล็ก ในการสังเคราะห์เป็นตัวดูดซับในรูปแบบเม็ดขนาดเล็ก สำหรับการขจัดอาร์เซนิกอนินทรีย์ในน้ำ ตรวจสอบลักษณะทางกายภาพของตัวดูดซับที่สังเคราะห์ได้ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) เทคนิคเอ็กซ์เรย์ฟลูออเรสเซนซ์ (XRF) และการย่อยตัวดูดซับด้วยกรด พบว่าตัวดูดซับเป็นแบบอสัณฐาน ไม่มีความเป็นรูพรุน และมีองค์ประกอบส่วนใหญ่คือ คาร์บอน ไนโตรเจน ออกซิเจน และเหล็ก โดยปริมาณเหล็กที่เติมในตัวดูดซับจะมีปริมาณมากขึ้นเมื่อเพิ่มความเข้มข้นของเหล็กคลอไรด์ ศึกษาปัจจัยต่างๆที่ส่งผลต่อการดูดซับอาร์เซนิกในระบบแบบbatch ที่อุณหภูมิห้อง พบว่าภาวะที่เหมาะสมของการดูดซับ ได้แก่ ความเข้มข้นของเหล็ก(III)ในสารละลายซิงค์ เท่ากับ 0.7 mg/mL ค่าพีเอชของสารละลาย เท่ากับ 6 และเวลาที่ใช้ในการดูดซับ เท่ากับ 8 ชั่วโมงหรือมากกว่า ไอโซเทอร์มการดูดซับอาร์เซนิก(V) เป็นไปตามแบบจำลองของแลงเมียร์ และมีความสามารถในการดูดซับอาร์เซนิกสูงสุดเท่ากับ 1.95 มิลลิกรัมต่อกรัมของตัวดูดซับ ไอออนบางชนิดในสารละลายทำให้ประสิทธิภาพการดูดซับอาร์เซนิกลดลง โดยเฉพาะอย่างยิ่งไอออนที่มีโครงสร้างของออกซีแอนไอออน เช่น ฟอสเฟต คาร์บอเนตและซัลเฟต เป็นต้น ตัวดูดซับซิงค์เสริมเหล็ก(III) ใช้ในการขจัดอาร์เซนิกอนินทรีย์จากน้ำเสียและน้ำดื่มซึ่งให้ผลเป็นที่น่าพอใจเมื่อตัวอย่างไม่มีไอออนรบกวน ดังที่กล่าวมาข้างต้น

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SINEEPHAN THANAWATPOONTAWEE: REMOVAL OF INORGANIC ARSENIC FROM WATER USING IRON(III)-LOADED ZEIN BASED ADSORBENT. ADVISOR: ASST. PROF. NARONG PRAPHAIRAKSIT, Ph.D., CO-ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., 70 pp.

Zein protein, a by-product from agricultural industry, was modified with iron compound and prepared as adsorbent bead for the removal of inorganic arsenic in aqueous solution. The adsorbent was characterized by scanning electron microscope (SEM), x-ray fluorescence (XRF) and inductively coupled plasma-optical emission spectrometer (ICP-OES). The adsorbent was amorphous with non-porous surface and comprised mainly of carbon, nitrogen, oxygen and iron in proportion with the iron(III) chloride (FeCl_3) loading amount. Various parameters for arsenic removal in batch system were studied at room temperature. The adsorption process was conducted under the optimized condition such as 0.7 mg/mL of iron(III) loading concentration in zein solution, pH 6 and contact time of 8 hr. or longer. The adsorption of arsenic(V) by this adsorbent was fitted to Langmuir isotherm model with the maximum capacity of 1.95 mg/g. Certain co-existing ions, especially those containing oxyanion structure i.e. phosphate, carbonate and sulphate, can significantly diminish the arsenic adsorption efficiency. This iron(III)-loaded zein adsorbent was applied to remove arsenic from waste water and drinking water with satisfactory result for relatively clean samples but less so for samples containing interference ions as mentioned previously.

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LIST OF ABBREVIATIONS

%	=	Percent
°C	=	Degree celcius
w/v	=	Weigh by volume
µm	=	Microns
mg/g	=	Milligram per gram
mg/mL	=	Milligram per millilitre
mg/L	=	Milligram per litre
L/mg	=	Litre per milligram
g	=	Gram
M	=	Molar
cm	=	Centimeters
rpm	=	Revolutions per minute
mL	=	Millilitre

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

With the growing technology and demands in the market nowadays, the number of industrial factories have rapidly emerged and this consequently has led to one of the major critical environmental problems in water pollution. Living organisms including human are in risk of toxic chemicals and heavy metals from water contamination. Arsenic (As) is a well-known toxic element and is commonly found in natural water as well as wastewater from industries [1, 2]. The arsenic intake can result in serious threats to human health such as lesion of skin, lung, kidney, stomach, and brain [3, 4]. Therefore, the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) has established a minimum contaminant level (MCL) of arsenic in drinking water as below 0.01 mg/L [5], whereas the MCL of arsenic in wastewater from the industries restricted by the Ministry of Science and Technology of Thailand is 0.25 mg/L before releasing to the environment [6]. Hence, the removal of inorganic arsenic from water is a very important practice.

There are several commonly used methods to remove arsenic from the water, for example, oxidation-precipitation, coagulation-flocculation and filtration, ion exchange, membrane filtration and adsorption [7, 8]. Each of these techniques can reduce the arsenic level in water to a certain degree yet some of which require costly instruments and skilled operators. Among these techniques, the adsorption method is relatively simple, inexpensive, and effective, so it becomes one of the most popular methods for the removal of contaminants in water [9].

Many previous works have been conducted in an attempt to find a low cost adsorbent for the removal of arsenic from agricultural and industrial wastes as well as its by-product such as red mud [10], bone char [11], pine leaves [12], and hydrated ferric oxide-treated sugarcane bagasse [13].

Zein, a class of prolamine protein found in the endosperm of corn, is a by-product from the corn sugar industry. Zein is considered agricultural waste because of its insufficiency in nutritive value, however, it is used as a raw material in various applications of biodegradable plastic. Zein is a hydrophobic polymer that is insoluble in water; nonetheless, it is soluble in aqueous alcohol [14-16]. Based on its solubility, zein can be regarded as a potential candidate for a solid adsorbent for water samples. Therefore, zein was chosen in this work as a prospect material for the preparation of adsorbent that may be beneficial for the removal of arsenic in water.

1.2 Scope of the research

- To synthesize and characterize iron(III)-loaded zein bead and use it as an adsorbent to remove arsenic in water samples.
- To study parameters affecting the arsenic adsorption of the prepared adsorbent, including the initial concentration of iron(III), pH of the solution, contact time, adsorption isotherm and interferences.
- To compare the adsorption efficiency between iron(III)-loaded zein adsorbent and the adsorbent treated with thermal hydrolysis technique (THL).
- To apply the developed adsorbent and method to remove arsenic from real water samples.

1.3 Benefits of this research

The new adsorbent, iron(III)-loaded zein beads, was prepared and used as an alternative adsorbent for the removal of inorganic arsenic from water.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Properties of arsenic

Arsenic (As) is a metalloid element with high toxicity. Its natural features are silver-grey and brittle crystalline solid, odorless and tasteless. Arsenic is usually found in the earth crust as arsenic compounds or contaminated in the environment [1]. A list of key physical properties of arsenic is shown in Table 2.1.

Table 2.1 Physical properties of arsenic

Physical properties	Value
Atomic number	33
Molar atomic weight	74.9216 g.mol ⁻¹
Melting point	81.7 °C
Boiling point	613 °C
Density	5.727 g.cm ⁻³
Electronegativity	2.18

Arsenic can be found in various organic and inorganic forms as shown in Figure 2.1 and Table 2.2. They can appear in all three states: liquid, solid, and gas. Arsenic species are present in several oxidation states including As(-3) (arsine gas, AsH₃), As(0) (arsenic element), As(+3) (arsenite), and As(+5) (arsenate). However, in the environment, arsenic is mostly found as inorganic oxyanions, i.e. trivalent arsenite (AsO₃⁻) and pentavalent arsenate (AsO₄⁻) [1, 17].

Table 2.2 Arsenic species in the environment [18].

Name	Abbreviation	Formula/structure
<u>Inorganic arsenicals</u>		
Arsenious acid or arsenite	As(III)	As(OH) ₃
Arsenic acid or arsenate	As(V)	H ₃ AsO ₄
Methylated arsenicals		
Monomethylarsonous acid	MMAA ^{III}	As(OH) ₂ CH ₃
Dimethylarsinous acid	DMAA ^{III}	As(OH)(CH ₃) ₂
Monomethylarsonic acid	MMAA ^V	AsO(OH) ₂ CH ₃
Dimethylarsinic acid	DMAA ^V	AsO(OH)(CH ₃) ₂
<u>Organoarsenic Compounds</u>		
Arsenocholine		(CH ₃) ₃ As ⁺ CH ₂ CH ₂ O
Arsenobetaine		(CH ₃) ₃ As ⁺ CH ₂ COO ⁻
Arsenosugars		
Thioarsenates		

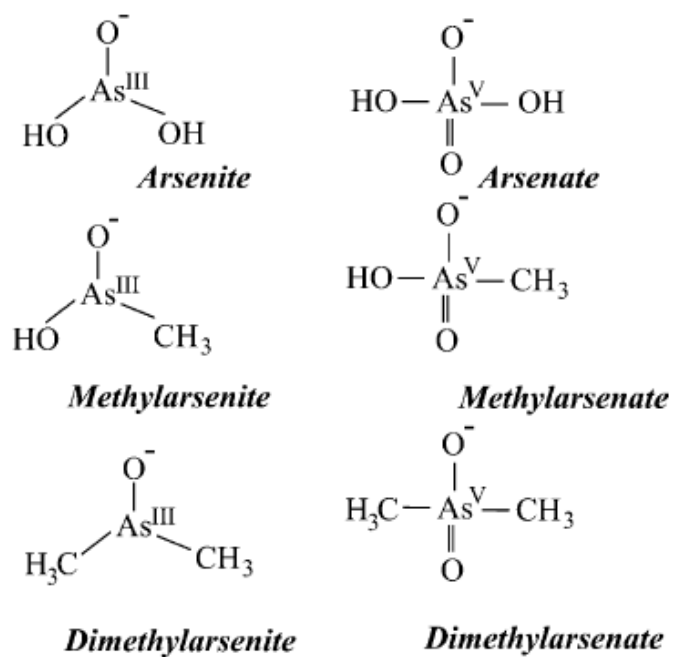


Figure 2.1 Arsenic species found in water [19].

Arsenic(III) is a hard acid that preferentially form complexes with oxygen and nitrogen, whereas arsenic(V) is more stable and likely to form complexes with sulfide [9]. Arsenic is sensitive to mobilization under oxidizing or reducing conditions. Thus, arsenite and arsenate are present in various species depending on pH of the solution [1, 20, 21]. The distribution of arsenic species as a function of pH is shown in Figure 2.2.

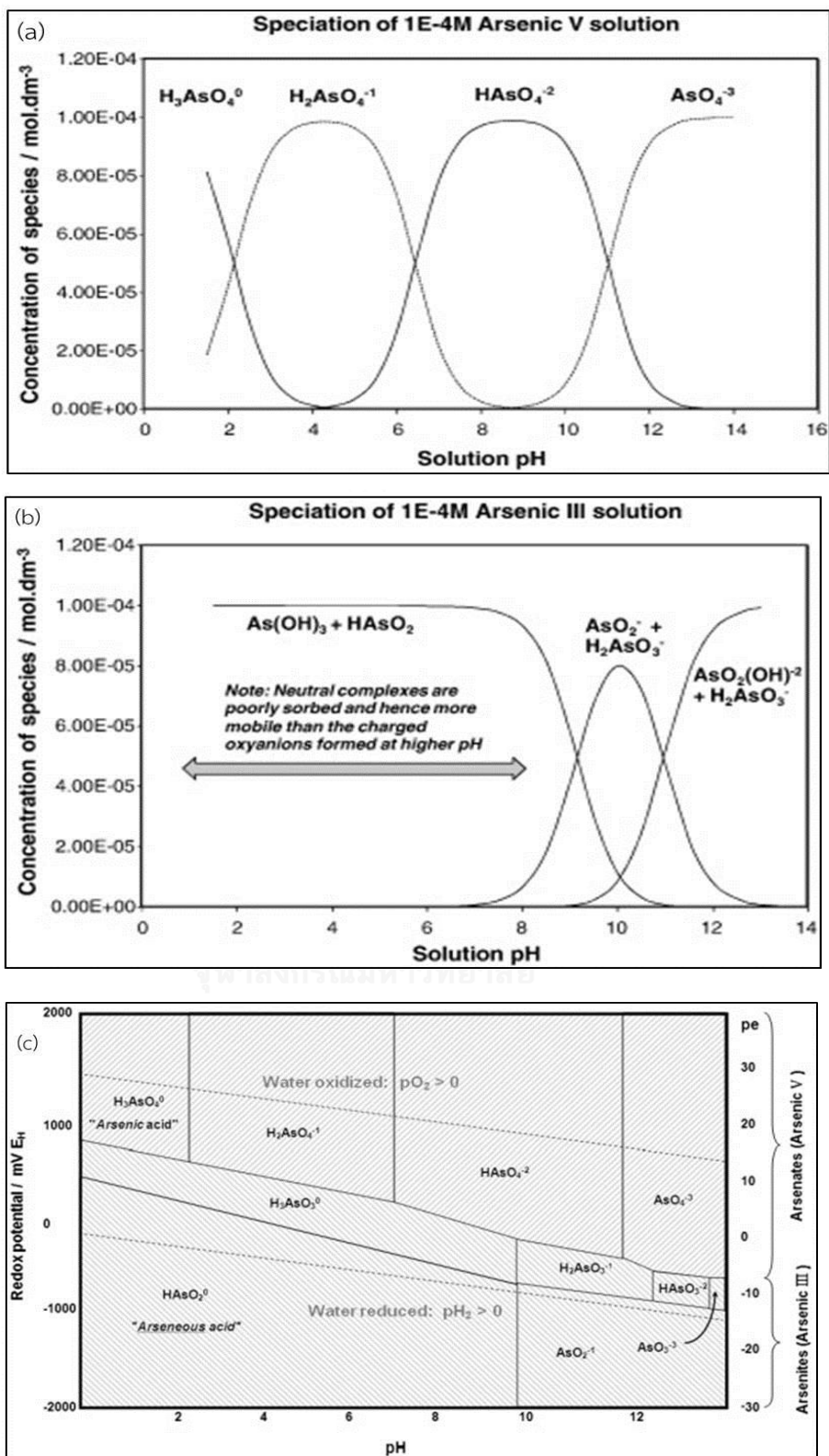


Figure 2.2 Distribution of (a) arsenic(V) and (b) arsenic(III) species at different pH and (c) redox potential diagram of arsenic [21].

2.1.2 Applications

Although its toxicity is a well-known and serious problem to human and environment, arsenic has various utility for human activities. For instance, arsenic compounds are frequently used in agriculture as pesticides, herbicides and crop desiccants. Arsenic is commonly used as feed additives for livestock as well as for the preservation of wood. In addition, arsenic is used in metallurgy to produce electric wires and electronic semiconductors. Other applications of arsenic include glass manufacturing and ceramic industries [22, 23].

2.1.3 Toxicity of arsenic

Contamination of arsenic is a critical problem in the world. Inorganic forms of arsenic, which are more harmful than the organic counterparts, are contaminated in the environment by the process of industries and even geochemical environments. Arsenic can be exposed to human by touching, eating, drinking, and smelling through arsenic-contaminated water or food and it is accumulated in tissues and body fluids. It can cause both acute and chronic health effects, for instance, skin lesions, muscle cramps, organ function disorders, gastrointestinal discomfort, cancers [4, 24, 25] and even death.

2.2 Methods for arsenic removal

As mentioned above, arsenic contamination in water is a serious threat to human and environment. The removal of arsenic is therefore necessary for humankind. A large number of techniques to remove arsenic have been established such as oxidation, coagulation-flocculation and filtration, ion exchange, membrane filtration, and adsorption. These methods are reviewed hereinafter.

2.2.1 Oxidation

Oxidation is a chemical reaction involving a process of adding oxygen atom to or releasing of electron from the compound thereby increasing the oxidation number of the compound. Arsenic(III) found generally in both wastewater and natural water is difficult to remove because it is present in a non-charged form under the pH lower than 9. Therefore, this oxidation technique has to be combined with other techniques for arsenic removal, for example, oxidation-precipitation [26], oxidation-filtration [27], and oxidation-coagulation [28]. The effective oxidants for oxidizing arsenite to arsenate are potassium permanganate, sodium hypochlorite and monochloramine [29].

2.2.2 Coagulation-flocculation and filtration

Although coagulation and flocculation are verisimilitudinous and they are often used interchangeably, they are different in the process. Coagulation is a process that colloidal particles and fine suspensions are destabilized and then begin to agglomerate, while flocculation refers to a next step after coagulation that the destabilized particles are conglomerated.

Colloids are small particles, with a size in the range of 10^{-9} - 10^{-6} meters, dispersed in the solution such as inorganic and organic arsenic compounds in wastewater. Coagulation-flocculation and filtration is an effective technique commonly used for the removal of arsenic in water. Because colloidal suspension does not naturally settle as sediment, the colloids are agglomerated through coagulation process. Coagulation is a process to combine between suspensions and colloids in the media by adding a chemical coagulant to promote destabilization. Commonly used coagulants are aluminium sulfate, ferric chloride, ferric sulfate, etc. The negatively charged ions of colloids and suspensions are neutralized by electrostatic attachment. Inorganic arsenic can be adsorbed onto coagulated floc, and then constantly grown into larger particles. After that, the unstable particles are removed from water via filtration technique. The efficiency of arsenic removal

depends on pH value, type of chemical coagulant, coagulant dosage, and composition of water, all of which are very important factors [30].

2.2.3 Ion exchange

Ion exchange process is one of the water treatment methods referring to a reversible chemical reaction of replacing between the contaminated ions in water and other similarly charged ions attached on immobile solid particles. This method is regularly used for arsenic removal in water by running the arsenic-contaminated water through a commercial ion exchange resin. The removal efficiency depends on selectivity and characteristic of resin. Ion exchange resins can be classified into two types: cation and anion exchangers that have positively charged ions and negatively charged ions, respectively [31].

Some techniques for are required as a pretreatment step prior to ion exchange process for the arsenic removal in water. For example, filtration is used to eliminate organic compounds, suspension and other contaminants for improvement of arsenic removal efficiency. Another technique that may be necessary is oxidation. Because non-charged forms of arsenic cannot be removed by ion exchange, the oxidation process is very beneficial for transformation of non-charged arsenic to charged species such as arsenite or arsenate. Furthermore, ion exchange resin can be regenerated by washing with NaCl solution.

2.2.4 Membrane filtration

Membrane filtration technique is used in water treatment for isolating any particles by water pressure driven through a membrane. Particles can be filtered by semi-permeable property of the membrane. The membrane filtration methods can be classified by the pore size of the membrane such as microfiltration membrane (MF), ultrafiltration membrane (UF), nanofiltration membrane (NF), and reverse osmosis (RO).

The removal efficiency of arsenic in water is subject to arsenic species and properties of the membrane used. Of all the membrane filtration methods, NF and RO are widely used for decreasing arsenic level in water because they show highly effective results [32, 33]. Nevertheless, these techniques are usually expensive and thus are suitable for only some specific applications including a water-purification, desalination, specific ions removal, etc.

2.2.5 Adsorption technique

Adsorption refers to a two-phase partitioning between the adsorbents existing on surface of solid or liquid substrate and the adsorbates that are target substances such as ions, atoms and molecules. Adsorption is a process of accumulation of analytic components passing through the interface of adsorbent. Adsorption method can be used in physical, biological and chemical systems, and it is the most popular technique used in industrial applications especially separation and purification of bulk chemicals and water purification. This technique is not only effective, highly reliable, easy to operate, but the adsorbent can also be obtained from various sources (natural, commercial, synthetic) and its adsorption property can be designed to fit individual work and can be regenerated. Accordingly, adsorption is a desirable technique for the removal of arsenic from aqueous samples and wastewater.

2.3 Adsorption

Adsorption procedure is generally elucidated by the following consecutive steps.

- I. External diffusion: analytes from a bulk solution are transferred to the external surface of an adsorbent by diffusion.
- II. Intraparticle diffusion or pore diffusion: analytes from the surface migrate into the porous of the adsorbent.

III. Adsorption of analytes on active site in the pore of the adsorbent.

The efficiency of adsorption process is dependent of the pore size, surface area, particle size of analyte, contact time, temperature, pH and the concentration of the solution.

2.3.1 Type of adsorption

Adsorption is a surface phenomenon that results from interactive forces between the adsorbate molecules in liquid phase and the adsorbent surface (typically solid). Such interactive force is an important factor for describing the adsorption mechanism. Hence, the adsorption process is generally classified into two mechanisms: physisorption (physical adsorption) and chemisorption (chemical adsorption).

Physical adsorption

Physical adsorption or physisorption is an adsorption mechanism that a substance adheres to the surface of adsorbent via the Van der Waals force (intermolecular force) which consists of London dispersion force and electrostatic force. Physical adsorption can occur as multilayer of the substance and the thickness of the layers can be increased by adding higher concentration of the substances. In addition, physical adsorption is a reversible process.

Chemical adsorption

Chemical adsorption or chemisorption has an adsorptive characteristic as chemical bonding. The chemical interaction between an adsorbate molecule and the interface of an adsorbent surface are sharing of electrons and binding via functional group. In contrast to the physical adsorption, the substance can adhere directly on the adsorbent's surface and form a monolayer. This is a specific process

which can occur on some solid surfaces, thus chemical adsorption is generally not reversible [34].

2.3.2 Adsorbents

As mentioned above, an adsorption is a process in which an adsorbing material adsorbs substances or analytes by either chemical or physical interaction. Adsorbents are used in adsorption techniques as a solid phase which has attractive and selective interaction with a molecule of analytes. Adsorbent can be divided by their sources: a natural adsorbent, a commercial adsorbent and a low-cost adsorbent.

- I. Natural adsorbent: there are many kinds of natural adsorbent used at present such as zeolite, clay, peat moss, chitosan, red mud, fly ash, etc. Some of natural sorbent are easy to find because of its high natural abundance [35].
- II. Commercial adsorbent: this type of adsorbents can be classified into three classes. The first group is “oxygen-containing adsorbent” that consist of hydrophilic and/or polar compounds namely silica gel and zeolite. Next, a hydrophobic and/or non-polar compound is named a “carbon-base adsorbent” including activated carbon and graphite. The last type is a “polymer-based adsorbent” which has several functional groups of both polar and non-polar on the porous polymer.
- III. Low-cost adsorbent: this is commonly used for any adsorption methods in wastewater. The materials used as low-cost adsorbents are usually by-products and wastes from agriculture or industries. A variety of materials, which are available in a large number and no economic value, can be used in adsorption techniques such as coconut shell, rice husk, sludge [36].

Modification of adsorbent

The adsorption techniques are usually used for the removal of contaminated water and wastewater. A low cost adsorbent, such as waste or by-product from agriculture or industries, is an interestingly good choice in both economical and environmental perspectives. However, the efficiency of some of these adsorbents are not sufficient for arsenic removal in water. Some of their weaknesses include a long contact time, low adsorption capacity, and no selectivity. The effectiveness of adsorbents depend largely on its surface characteristics such as specific surface area, functional group, pore size and pore volume, hence, certain modifications are required to improve its adsorption efficiency. The modifications of adsorbent can be categorized into two types: physical modification and chemical modification. The choice of modification method depends upon the starting material and adsorbate substance.

Physical modification

The physical modification is a modification method to improve or reform the physical properties of the adsorbent material. The properties such as specific surface area, pore volume and pore diameter, can be changed via physical modification, whereas some of chemical modifications can reduce the internal surface area and pore volume. The physical modification method commonly used is thermal or heat treatment. Thermal treatment not only reduces volume and mass of adsorbent but also modifies adsorbent which has outstanding physical characteristic including transformation of the structure of adsorbent, increasing their porous and surface chemistry [37]. Accordingly, the thermal treatment leads to change in better efficiency for the removal of target substances [38].

Chemical modification

Adsorption mechanism depends on types and characteristics of adsorbent's surface because chemical species can be mostly adsorbed by the presence of functional groups of adsorbent surface. Some of the surface functional groups, for instance, carboxylic, hydroxyl and lactone have high affinity to form complex with metals and thus improve its metal removal ability. To enhance this chelating efficiency, chemical modification was more regularly used as pretreatment processes because this method can activate or reform functional groups of the adsorbent surface through certain processes such as removing organic matter in adsorbent, improving chelating binding sites, removing or masking functional group and increasing surface area. The chemical modification can be classified into three types: acidic treatment, basic treatment, and impregnation method [39].

Acidic treatment

This is a pretreatment process to enhance acidic property via functional groups on the adsorbent's surface. Commonly used chemical reagents for an acidic treatment are hydrochloric acid, nitric acid, sulfuric acid, citric acid, etc. The acid treatment is the most well-known method of protonation because it is a simple method to create more positive charge density on the adsorbent surface that can interact with negative charged species of contaminated substances in water via electrostatic force [40]. In addition, acid treatment not only can enlarge the pore but also can increase the surface area that improves the adsorption capacity of the acid-treated adsorbent [41]. However, in some cases of using high concentration of acid, the active sites of the adsorbent were protonated as positive charge that metal ions in the solution prefer to remain in the aqueous solution than to be adsorbed on the adsorbent surface.

Basic treatment

The basic treatment is beneficial in some adsorption methods, especially an adsorption of metal ions from aqueous solution. The modifying reagents, which are commonly used for basic treatment, are sodium hydroxide, calcium hydroxide, sodium carbonate, etc. After the basic treatment, protons of functional groups on the adsorbent surface are released and reacted with hydroxide ions from the reagent, and then acidity of the surface decreases. The surface adsorbent becomes more negatively charged and preferentially attracted to positive ions [42].

Impregnation method

Impregnation method is one of the simple modification methods by immersing the adsorbent material into a suitable chemical including molecules, ions, chelating agents and modifying agents that provide better affinity between target species and the adsorbent. These chemicals (impregnating agents) provide desired functional groups and/or other properties on the adsorbent surface that in turn promote the synergism between adsorbent and target species. Nevertheless, the properties of impregnated adsorbent depend on various factors such as the concentration of impregnating agent, impregnation time, surface area, pore volume and active site of adsorbent [43].

2.3.3 Adsorption isotherm

In adsorption phenomenon, substances can be adsorbed and desorbed all the time and continuously until the adsorption and desorption are in equilibrium where the concentration of adsorbed substances on the surface does not change. This state is called adsorption equilibrium and it can be described by adsorption isotherm. Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at constant

temperature. The widely accepted adsorption isotherms for adsorption process are the Langmuir isotherm and the Freundlich isotherm [44].

2.3.3.1 Langmuir adsorption isotherm

The Langmuir isotherm is a model used to explain a monolayer adsorption of adsorbed species on the adsorbent surface at a constant temperature. The adsorbate molecules are adsorbed with the limitation of the number of active sites via chemical adsorption, by which all of adsorbate molecules are adsorbed with the same mechanism. The Langmuir isotherm is described by Equation 2.1.

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (2.1)$$

where C_e = the equilibrium concentration of analyte in the solution (mg/L)

q = the adsorption capacity of adsorbent (mg/g)

q_m = the maximum capacity of the adsorbent (mg/g)

b = the constant related to the affinity of binding site (L/mg)

Plotting $\frac{C_e}{q}$ value (y axis) versus C_e (x axis), q_m and b can be calculated from the slope and y-intercept as shown in Figure 2.3.

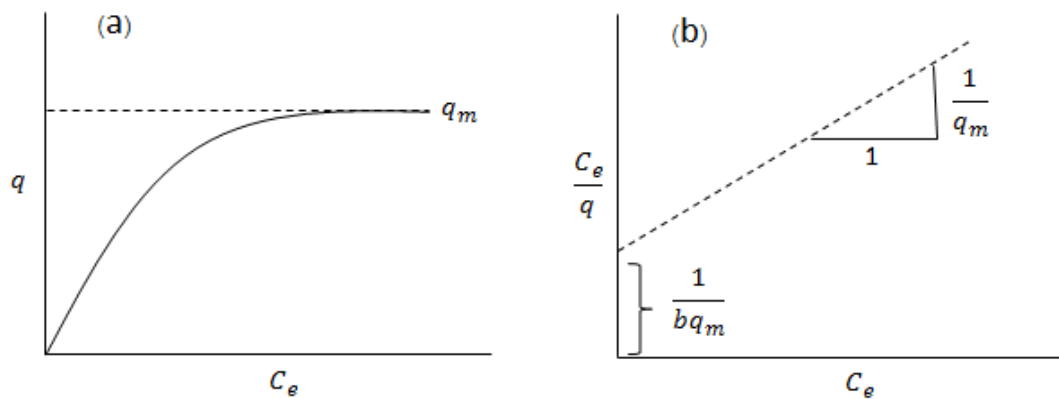


Figure 2.3. (a) adsorption isotherm of a monolayer adsorption (hypothetical system) and (b) Langmuir adsorption isotherm.

2.3.2.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm can be applied to describe the multilayer adsorption and heterogeneous surface. The Freundlich equation is shown in the following equation.

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (2.2)$$

where K_f = the constant related to adsorption capacity (mg/g)

n = the Freundlich constant

C_e and q are the same parameters in the Langmuir adsorption isotherm. Plotting $\log q$ versus $\log C_e$, gives a linear graph with the slope of $\frac{1}{n}$ and y-intercept of $\log K_f$ as shown in Figure 2.4.

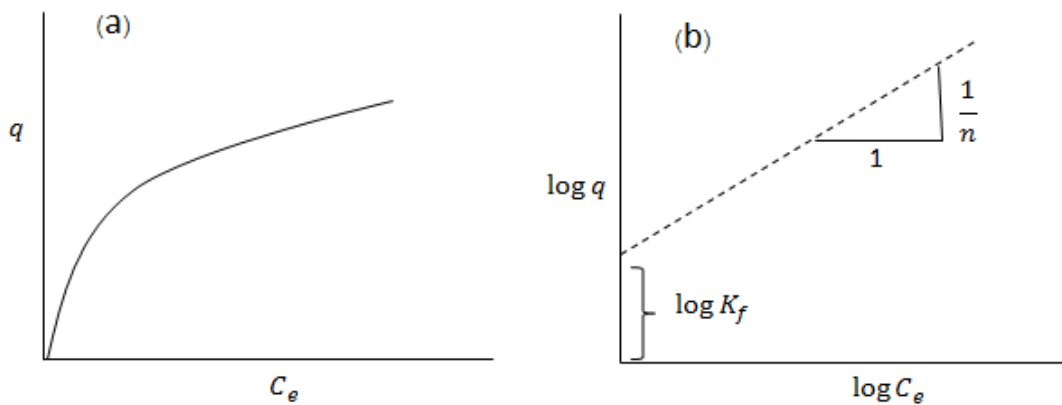


Figure 2.4 (a) adsorption isotherm of a multilayer adsorption (hypothetical system) and (b) Freundlich adsorption isotherm.

2.4 Zein protein

Zein, a major protein in the endosperm of corn, is very useful as nitrogen source for an embryo. This protein is a mixture of different peptides that have various molecular sizes, solubility and charges [14, 45]. Zein proteins belong to the prolamine protein which are particularly rich in lucine, proline, glutamine, and alanine. Zein proteins are insoluble in pure water or pure ethanol because their molecules contain a low amount of polar amino acid with a high proportion of nonpolar amino acid. Zein is a heterogeneous mixture of disulfide-linkage. The other physical properties of zein proteins are shown in Table 2.3.

Table 2.3 Physical properties of zein protein [14].

Physical properties	Characteristics
Bulking value	0.805 L/kg
Color	Light cream
Dielectric constant (500V, 60 cycles, 25-90°C)	4.0-5.0
Diffusion coefficient	$3.7 \times 10^{-14} \text{ m}^2/\text{s}$
Einstein viscosity coefficient	25
Glass transition temperature	165 °C
Isoelectric point	pH 6.2 (varies 5 to 9)
Molecular weight	35 kDa (varies 9.6 to 44 kDa)
Partial specific volume	0.771
Physical form	Amorphous powder
Sedimentation coefficient	1.5 s
Specific gravity, at 25°C	1.25
Thermal degradation point	320 °C

Zein is obtained as by-products in corn-sugar industry and starch production by wet milling. Zein is devoid of some essential amino acids such as tryptophan and lysine that is necessary for normal growth. Hence, zein has poor nutritive value for human food products. Natural characteristics of zein are tough, glossy and resistant to microbial attack; therefore it is used in various industries, particularly food and pharmaceutical industry. Zein can form several structures including film, microsphere, fiber, nanoparticle, encapsulated particle, composites and other polymers. In addition, zein is biodegradable and renewable that gives environmental benefit [36, 46].

2.5 Literature review

There are a variety of contaminant removal techniques, but most of them are expensive and complicated methods. Adsorption is an attractive and cost effective technique for the removal of certain metals from aqueous solution, for example, a method to remove contaminated arsenic in water media.

2.5.1 Removal of arsenic from water by using a low cost adsorbent including zein

The ideal adsorbent should be effective, inexpensive and easy to prepare. The most widely used adsorbent is low cost materials. These adsorbents are derived from plentiful sources such as natural source, local available source, co-product and waste from industry/agriculture. There are many reports about arsenic removal by low cost adsorbents, some of which are summarized below.

Maji et al [47] developed laterite soil, a natural adsorbent, for eliminating arsenic from ground water by adsorption method in batch and column operations. In the batch operation, laterite soil can remove arsenic up to 98% from the samples. The correlation coefficient of adsorption isotherm follows both Langmuir and Freundlich models and the adsorption mechanism is pseudo second-order reaction. In the column operation, the breakthrough time was 6.75 hours.

Shah Saqib et al [48] presented arsenic remediation from aqueous solution by using three different wastes: blue pine wood shaving, walnut shell and chick pea testa. It was found that the arsenic removal from drinking water of blue pine wood (>90%), walnut shell (88%) are effective, on the other hand, the result from using chick pea testa was not as efficient. The report showed that the blue pine is the most effective adsorbent with the obtained isotherm following both Langmuir and Freundlich models.

Li et al [49] selected red mud, a by-product of alkaline-leaching of bauxite, as adsorbent to remove arsenic in aqueous solution. The red mud was modified by ferrous and ferric solution to improve adsorption capacity. The result

showed that ferrous-modified red mud gives better results than using ferric-modified red mud and unmodified red mud. The removal of arsenic was obtained at 91% within 24 hours from an initial arsenic concentration of 0.2 or 0.3 g/L.

Xu et al [50] conducted a comparative study between hollow zein nanoparticles and solid zein nanoparticles to remove reactive dye. The results showed that the hollow zein nanoparticles are more effective than the solid nanoparticles. Under the optimized condition, the maximum capacity derived from Langmuir adsorption isotherm was 1016.0 mg/g. The outcome of hollow zein nanoparticle is also higher than other biodegradable adsorbents, for instance, activated carbon, microalgae, high lime fly ash, etc.

Zein proteins are normally used as biodegradable materials in industrial applications, and there are a few reports that use zein in adsorption techniques. Therefore, it is a challenge to apply zein proteins as an adsorbent or solid support for arsenic adsorption.

2.5.2 Iron(III) for arsenic removal

Iron is a silver-grey and glossy element and its compounds are commonly found around the world. Iron is a metallic element that can exist in a wide range of oxidation stage from -2 to +6; however, its oxidation numbers are generally found to be +2 and +3. The key properties of iron are shown in Table 2.4.

Table 2.4 Physical properties of iron

Physical properties	
Atomic number	26
Molar atomic weight	55.847 g.mol ⁻¹
Melting point	1538 °C
Boiling point	2862 °C
Density	7.874 g.cm ⁻³
Electronegativity	1.83

Iron compounds have been used for the removal of heavy metals, especially arsenic in aqueous solution [51-55]. The methods are continuously developed because iron compounds are readily available and they show effectiveness for reducing heavy metal levels in water. Iron and iron compounds applied for the removal of heavy metals in aqueous solution were used in several forms, for example, iron hydroxide, iron oxide, hematite, iron(III) and zero-valent iron (ZVI), etc.

Gupta et al. [56] used zero-valent iron for the removal of total inorganic arsenic in water by encapsulation of the arsenic into chitosan nanospheres. The adsorbent was then characterized by FT-IR, SEM-EDX, BET, and XRD. The results showed that the highest adsorption capacity was found at pH 7 with 94 and 119 mg/g for arsenite and arsenate, respectively. The interferences such as sulphate and phosphate interfere partly. The adsorption followed Langmuir isotherm model. The chitosan zero-valent nanoparticles can be reused for five cycles with 0.1 M NaOH.

Sheng et al. [57] reported the As(V) removal from aqueous solution by using the iron(II) coated honeycomb briquette cinders adsorbent. The adsorption isotherm fitted Langmuir model, and the capacity of the adsorbent at pH 7.5 was 961.5 µg/g. Some of the interference ions decreasing the adsorption efficiency were

$\text{PO}_4^{-3} > \text{HCO}_3^- > \text{F}^- > \text{Cl}^-$. This adsorbent demonstrated a monolayer adsorption with good capacity.

Zhao et al. [58] synthesized iron(III)-loaded ligand exchange cotton cellulose (Fe(III)LLECC) for the removal of arsenic in drinking water. The adsorbent is inexpensive and biodegradable, moreover, it is highly selective toward arsenic(V). The Fe(III)LLECC is independent of pH in a relatively wide range and it provided a monolayer adsorption. In column study, it preserved 83% of the original saturation adsorption capacity.

Lunge et al. [59] evaluated the ability of using magnetic iron oxide nanoparticles from tea waste. The characterization of this sorbent was performed by SEM, TEM, and XRD. For the removal of arsenic(III) and arsenic(V), the isotherm fitted the Langmuir adsorption model and the capacities at pH 7 were 188.69 mg/g and 153.8 mg/g for arsenic(III) and arsenic(V), respectively. The kinetic model of the arsenic(III) adsorption on magnetic iron oxide nanoparticles was fitted to a pseudo second-order reaction. However, some anions can affect the adsorption capacity. On the other hand, it is a cheap adsorbent and also can be reused up to 5 cycles.

Yadav et al. [60] demonstrated the adsorption of arsenic from water by using bagasse fly ash-iron coated (BFA-IC) and sponge iron char (SIC) as adsorbents. The surface area of BFA-IC and SIC as determined by BET method were 168 and 78.63 m²/g, respectively. In batch operation, the equilibrium data fitted to Langmuir Freundlich, Temkin and Redlich-Peterson models. Langmuir adsorption isotherm was used to estimate the maximum arsenite adsorption capacity (q_m) as 39.83 µg/g (BFA-IC) and 27.85 µg/g (SIC) while arsenate adsorption capacity were 25.82 µg/g (BFA-IC) and 28.58 µg/g (SIC). In addition, the kinetic adsorption was best fitted to pseudo-second order model. The arsenic(III) adsorption on BFA-IC was best achieved at pH 7, whereas those of arsenic(V) on BFA-IC and SIC were optimal at pH 12.

Based on these findings, this work aims to develop a new low-cost adsorbent using iron(III) for the removal of inorganic arsenic in aqueous solution and

to study the efficiency of this adsorbent in comparative to those treated with thermal hydrolysis method.



CHAPTER III

EXPERIMENTAL

3.1 Analytical instruments

Table 3.1 Instrument list.

Instruments	Model, Manufacturer
Inductively coupled plasma optical emission spectrometer	iCAP 6500 DUO, Thermo Scientific
Fourier transformed infrared spectrometer	NICOLET 6700, Thermo Scientific
Scanning electron microscope	JSM-5410LV, JEOL
Scanning electron microscope with energy dispersive x-ray spectrometer	JSM-6610LV, JEOL
X-ray fluorescence spectrometer	XDV-SDD, Fischer
X-ray diffraction spectrometer	Dmax-2200 Ultima ⁺ , Rigaku
pH meter	UltraBASIC-10, Denver
Multi-position hotplate stirrer	KIKA- WERKE
Sonicator	CREST
Vacuum pump	Vacubrand

The Inductively coupled plasma optical emission spectrometer (ICP-OES) was used to measure the concentration of arsenic in the solutions. The conditions operated in this work are shown in Table 3.2

Table 3.2 Conditions of ICP-OES for the As determination.

Conditions	Values
RF power	1150 W
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.6 L/min
Coolant gas flow	12 L/min
Flush pump rate	50 rpm
Pump stabilization time	5 s
As emission wavelength	180.42 nm
Replicate	3

3.2 Chemicals

All chemicals used in this work were analytical grade as listed in Table 3.3.

Table 3.3 Chemicals list

Chemicals	Supplier
Ethanol	Merck
Ferric chloride	Sigma-Aldrich
Hydrochloric acid 37%	Merck
Nitric acid 65%	Merck
Sodium arsenate dibasic heptahydrated	Sigma-Aldrich
Sodium arsenite	BDH Chemicals
Sodium chloride	Carlo Erba
Sodium hydroxide	Merck
Sodium phosphate	BDH Chemicals
Sodium hydrogen carbonate	Merck

Sodium nitrate	Fluka
Sodium sulphate	Carlo Erba
Potassium permanganate	Sigma-Aldrich
Zein powder	Sigma

3.3 Synthesis of iron(III)-loaded zein-based adsorbents

Iron(III)-loaded zein-based adsorbents were synthesized by mixing iron(III) chloride and 50%(w/v) zein solution by the following procedure. First, a zein solution was prepared by dissolving zein powder in 70% ethanol [61]. Then a stock solution of 100 mg/mL FeCl_3 was added with various volumes to obtain final concentrations of iron(III) in the range of 0.1-7.0 mg/mL; the solution color turned from wheaten yellow to dark brown. Next, 0.2 mL of 1 M NaOH was added into the mixing solution under vigorous stirring. After that, the homogeneously mixed solution was dropped into deionized water at 5 °C by a plastic syringe (with needle no.29) under continuous stirring at 650 rpm. Iron(III)-loaded zein-based adsorbent beads were formed in this cold water. The beads were filtered and then dried overnight at room temperature (25 ± 2 °C). Finally, the adsorbent beads were sieved to obtain a particle size of lower than 1.40 mm, and then kept in a dry bottle until further use.

3.4 Preparation of solutions

Arsenic(III) solution (arsenite solution)

Arsenic(III) solution was prepared in a concentration of 1000 mg/L by weighing exactly 86.7 mg of sodium arsenite then dissolving it with deionized water using 50.0 mL volumetric flask. The arsenite solution was kept in a plastic bottle in a dry place.

Arsenic(V) solution (arsenate solution)

Arsenic(V) solution was prepared in a concentration of 1000 mg/L with a total volume of 50.0 mL. A 416.45 mg of sodium arsenate dibasic heptahydrate was exactly weighed, and then dissolved and made up to the volume with deionized water. The arsenate solution was kept in a plastic bottle in a dry place.

FeCl₃ solution

Ferric chloride solution (100 mg/mL, 10.0 mL) was prepared by dissolving 344.6 mg of ferric chloride with deionized water. It was sonicated for 1 minute before use.

Hydrochloric acid

Hydrochloric acid solution was prepared in a concentration of 1 M by dilution of concentrated Hydrochloric acid (37%) with deionized water.

Sodium hydroxide solution

Sodium hydroxide solution was prepared in a concentration of 1 M by dissolving an appropriate amount of sodium hydroxide in deionized water.

3.5 Characterization of the adsorbent

3.5.1 Iron content

The acid digestion was used to transform the adsorbent beads into a solution before the determination of iron content by ICP-OES. Approximately 0.50 g of iron(III)-loaded zein-based adsorbents were weighed and 10 mL of concentrated HCl was added into a beaker. The beaker was covered with watch glass, and then

placed on a hotplate. The mixture solution was refluxed at 95 ± 5 °C for 15 minutes and was consecutively filtered by a filter membrane no. 41 twice. After that, the final volume was made up to 50 mL with deionized water. The whole digestion process was performed in a fume hood [62]. In addition, the digested sample was 100-fold diluted and filtered by 0.45 μm nylon syringe filter before analysis by ICP-OES.

3.5.2 Fourier transform infrared spectroscopy (FT-IR)

FT-IR analysis was used for the identification of the reactive sites or functional groups on the iron(III)-loaded zein-based adsorbent. The result was compared with those obtained from the adsorbent treated by thermal hydrolysis method. The spectra were recorded from 600 to 4000 cm^{-1} using attenuated total reflectance mode (ATR).

3.5.3 Scanning electron microscope with energy dispersive x-ray spectrometer (SEM-EDX)

SEM has the ability to characterize surface and morphology of the adsorbents. The magnifications used for studying iron(III)-loaded zein based adsorbent were 50X and 1500X. The SEM-EDX not only can show the morphology, but also can analyze elements in the adsorbents.

3.5.4 X-ray fluorescence spectroscopy (XRF)

XRF is one of non-destructive techniques used for the investigation of elemental composition in a sample. In this work, XRF was used for the determination of iron in the adsorbents. The zein-based adsorbents initially loaded with iron(III) in the concentration range of 0.1 – 7.0 mg/mL were analyzed, and then the amount of iron in the adsorbent was calculated as a percentage relative to the total amount of elements.

3.5.5 X-ray diffraction spectroscopy (XRD)

X-ray diffraction spectroscopy is a non-destructive technique consisting of a monochromater and a Cu K-alpha radiation source that can be operated under 40 kV and 30 mA. XRD can provide information about the crystallographic structure of the adsorbent and its chemical compounds. It can reveal the differences between the structures of zein, the iron(III)-loaded zein-based adsorbent, and the adsorbent treated by thermal hydrolysis method.

3.6 Adsorption of arsenic(V) by iron(III)-loaded zein-based adsorbent

Arsenic adsorption was carried out by mixing 10 mL of arsenate solution with approximately 0.1 g of adsorbent (the exact weight was noted), and then stirring the mixture at 300 rpm under room temperature (25 ± 2 °C). The pH was adjusted to the desired value by 1 M HCl or 1 M NaOH. After the adsorption process, the sample was filtered through a 0.45- μ m nylon syringe filter membrane. The filtrate was analyzed for the remaining arsenic content by ICP-OES. The amount of adsorbed arsenic was calculated by the following equation,

$$Q_e = (C_0 - C_e) \times \frac{v}{w} \quad (3.1)$$

Where

Q_e is the amount of adsorbed arsenic (mg/g)

C_0 is the initial concentration of arsenic (mg/L)

C_e is the equilibrium concentration of arsenic (mg/L)

v is the volume of the solution (L)

w is the dose of adsorbent (g)

The percentage of arsenic removal was calculated using the following equation,

$$\% \text{removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (3.2)$$

3.6.1 Effect of iron(III) concentration

The effect of iron(III) concentration for loading into the adsorbent was investigated to maximize the arsenic removal. In the preparation of adsorbent beads, 50% w/v zein solutions were mixed with FeCl₃ solutions with various initial concentrations, i.e. 0.1, 0.3, 0.5, 0.7, 1.0, 2.5, 4.0, 6.0, and 7.0 mg/mL.

A 0.10 g of iron(III)-loaded zein-based adsorbent was added to 10 mL of 1.0 mg/mL arsenic(V) solution. The mixture was stirred at 300 rpm at room temperature (25 ± 2 °C) for 2 hours. The remaining arsenic concentration in the solution was determined by ICP-OES and the adsorption efficiencies were calculated according to equation (3.1) and (3.2). The optimum iron(III) concentration for the adsorbent preparation was determined by comparing the adsorption efficacy among these adsorbents.

3.6.2 Effect of pH

The effect of pH was investigated by varying the pH of 1 mg/L As(V) solution. The pH was adjusted in the range of 3-9 by 1 M NaOH and/or 1 M HCl. The initial iron(III) concentration for the synthesis of the adsorbent was fixed at 0.7 mg/mL. The 0.10 g of adsorbent was pH adjusted, mixed with 10.0 mL of As(V) solution and shaken with ~300 rpm speed at room temperature for 2 hours. The solution was filtered and the As(V) remaining in the solution was determined by ICP-OES. The adsorption efficiency was calculated by the similar method shown in the previous section.

3.6.3 Effect of adsorption time

In this work, the effect of adsorption time or contact time was optimized for the removal of As(V). A 0.10 g of adsorbent was used to remove As(V) from a 10 mL of 1 mg/L As(V) solution; the stirring speed was ~300 rpm. The solution was sampled at the intervals of 15, 30, 60, 120, 240, 480, and 960 minutes. Each of the sampled solutions were analyzed for the remaining As concentration in the solution by ICP-OES compared with the initial As concentration. The efficiency of arsenic adsorption was calculated by the same method as shown in the previous section.

3.6.4 Adsorption isotherm

Under the optimal condition for the removal of As(V), the adsorption isotherm was investigated at room temperature. A 0.10 g of iron(III)-loaded zein-based adsorbent was mixed with 10 mL of solution containing various initial As(V) concentrations of 0.5, 1, 10, 30, 50, 70 and 100 mg/L. The As(V) solutions were adjusted to pH 6 before the test. The mixture solutions were stirred with a speed of 300 rpm for 16 hours to ensure that the adsorption reach the equilibrium. After that the solutions were filtered and the filtrate was analyzed by ICP-OES. The results were fitted with Langmuir and Freundlich adsorption model in order to investigate its adsorption mechanism and the maximum adsorption capacity for arsenic removal.

3.6.5 Interferences

Practically, sample solutions do not contain only arsenic, but other common anions such as NO_3^- , Cl^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} are also found. The effect of interferences from these anions was studied by adding 1, 10, and 100 mg/L of each competing anions into 1 mg/L As(V) solution. Under the optimal condition, the adsorbent was weighted 0.10 g and soaked with each of the binary mixture solutions. Next, the mixture solutions were stirred (~300 rpm) at room temperature for 16 hours. The efficiency of arsenic adsorption was obtained by ICP-OES analysis.

3.7 Adsorption of As(III) by using iron(III)-loaded zein-based adsorbent

Firstly, the optimized parameters for As(V) removal were used for As(III) removal. A 0.10 g of adsorbent was used for testing with 10 mL of 1 mg/L As(III); the pH of the As(III) solution was 7. The adsorption time was used for 16 hours with stirring speed of ~300 rpm. All of the procedure was performed at room temperature. Finally, the efficiency of As(III) removal was obtained by ICP-OES similar to the method used for As(V) as mentioned above.

3.8 Adsorption of arsenic by the thermal hydrolysis-treated adsorbent

Thermal hydrolysis (THL) or forced hydrolysis technique is a simple technique for modification of adsorbent that can improve its adsorption efficiency. THL is a process that the temperature of a solution was increased in order to agglomerate colloidal oxide or hydroxide and then transform them to metal oxide nanoparticles. Nito-Degado and Rangel-Mendez [23] studied the arsenic adsorption in water by activated carbon modified with ferric chloride through THL. It was found that the iron nanoparticles obtained by THL technique can improve the adsorption capacity. Under the equilibrium condition, the adsorption isotherm was fitted with Freundlich isotherm model with the highest adsorption capacity of 3.25 mg/g.

3.8.1 Effect of temperature for THL

This work aims to improve the efficiency of the arsenic removal in aqueous solution by using iron(III)-loaded zein-based adsorbent treated with THL. A comparison of adsorption capability between THL-treated adsorbent and non-treated adsorbent was studied. Approximately 0.5 g of the iron(III)-loaded zein-based adsorbent was soaked in 25 mL of deionized water and refluxed in fume hood for 2 hours at various temperature of 60 °C, 80 °C, and 100 °C. After that, the solutions were filtered and washed with deionized water. The treated adsorbents were dried at 100 °C for 24 hours in an oven and then were kept in a desiccator.

The THL-treated adsorbent was used for arsenic removal under the same conditions as those optimized for non-treated adsorbent. A 0.10 g of THL-treated adsorbent was mixed with 1.0 mg/L of arsenic solution at pH 6 and then shaken (~300 rpm) for 16 hours. After that, the sample was filtered and analyzed by ICP-OES.

3.8.2 Characterization of THL-treated adsorbent

The amount of iron contained in the THL-treated adsorbent was investigated by acid digestion and ICP-OES. A 0.50 g THL-treated adsorbent prepared with various THL temperatures of 60 °C, 80 °C, and 100 °C was added into 10.0 mL of concentrated HCl. The beaker was covered with watch glass, and then placed on a hotplate at 95 ± 5 °C for 15 minutes for digestion. After that, the mixture was filtered and the volume was made up to 25.0 mL with deionized water. The solution was diluted 10 times and filtered with 0.45 μm nylon syringe filter prior to the analysis by ICP-OES.

3.9 Arsenic removal from real wastewater samples

The real wastewater samples, designated as TK-80 and TK-81, were obtained from the PTT Public Company Limited (Thailand). They were treated with iron(III)-loaded zein-based adsorbent for arsenic removal by the following procedure. First, the wastewater samples were filtered to remove any sediments. Excess amount of KMnO_4 was added into the samples and stirred for 15 minutes [29] to oxidize As(III) in the samples to As(V) in order to improve the arsenic adsorption efficiency. Next, the oxidized samples were filtered and the pH was adjusted to pH 6 before being used for arsenic adsorption. A 0.30 g of iron(III)-loaded zein-based adsorbent was added into 5 mL of each sample and stirred at 300 rpm speed for 16 hours. The remaining arsenic in the solution was determined by ICP-OES after filtration.

A Chulalongkorn University's pond water sample was also used to assess the arsenic removal efficiency of the developed adsorbent. The pond water sample was

filtered, spiked with 1 mg/L of As(V) and adjusted to pH 6 with 1 M NaOH solution and 1 M HCl. A 0.10 g of the adsorbent was added into the spiked sample and stirred with speed of 300 rpm. After stirring for 16 hours at room temperature, the remaining arsenic concentration was determined by ICP-OES.

In addition, three drinking water samples were chosen as real samples for this study. They were labelled as drinking water I, drinking water II and drinking water III. A 1 mg/L of As(V) solution was spiked into the samples and the appropriate pH was adjusted. Each drinking water sample was loaded with 0.10 g adsorbent in a beaker and the solutions were continuously stirred for 16 hours. After that, the concentrations of As(V) in the water samples were determined by ICP-OES.



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation and modification of adsorbent

Zein powder dissolved in 70% ethanol was a yellowish solution which became dark brown after the incorporation of iron(III). In this experiment, the adsorbents were synthesized by varying the iron(III) concentrations added to the zein solution. The iron(III)-loaded zein beads obtained exhibited different shades of brown color proportional to the amount of loaded iron as shown in Figure 4.1.

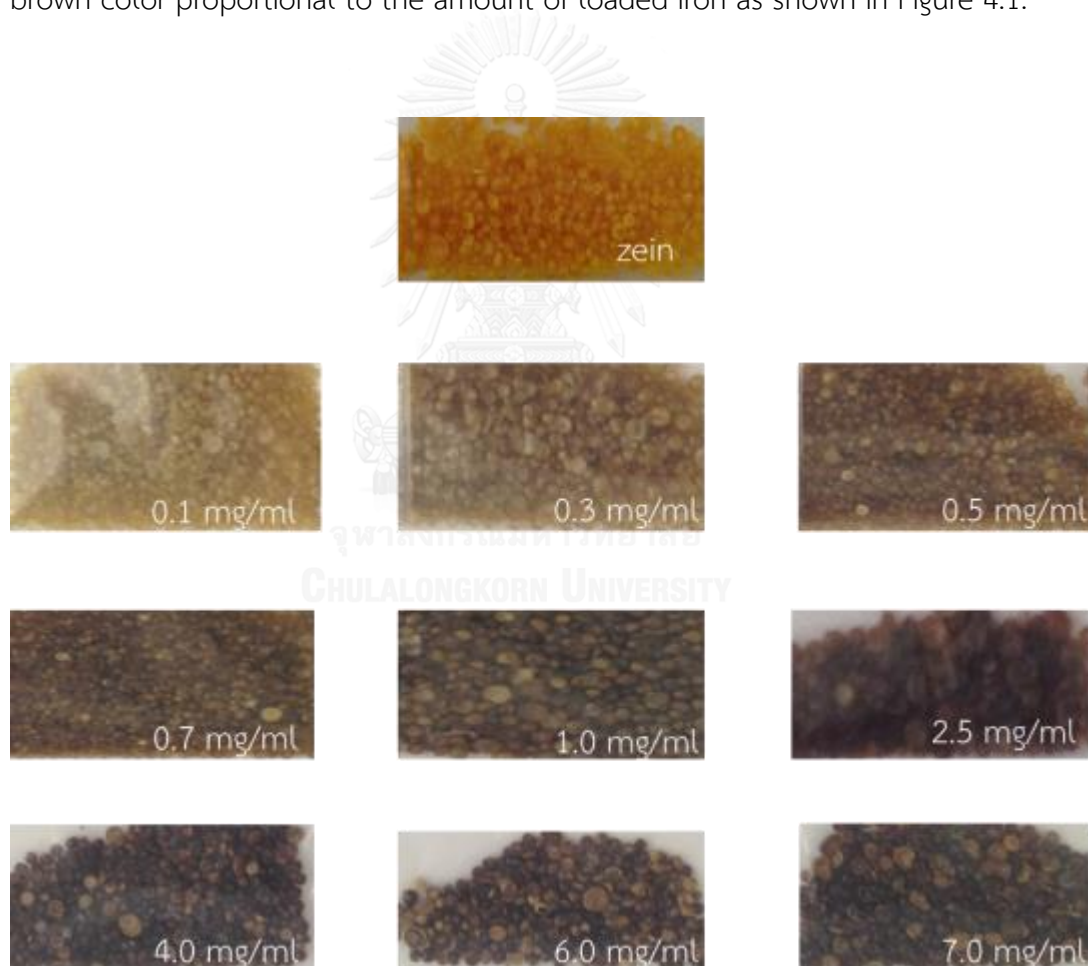


Figure 4.1 Iron(III)-loaded zein adsorbents obtained with different loading iron(III) concentration from 0.1 to 7.0 mg/mL.

4.2 Characterization of adsorbent

4.2.1 Iron content

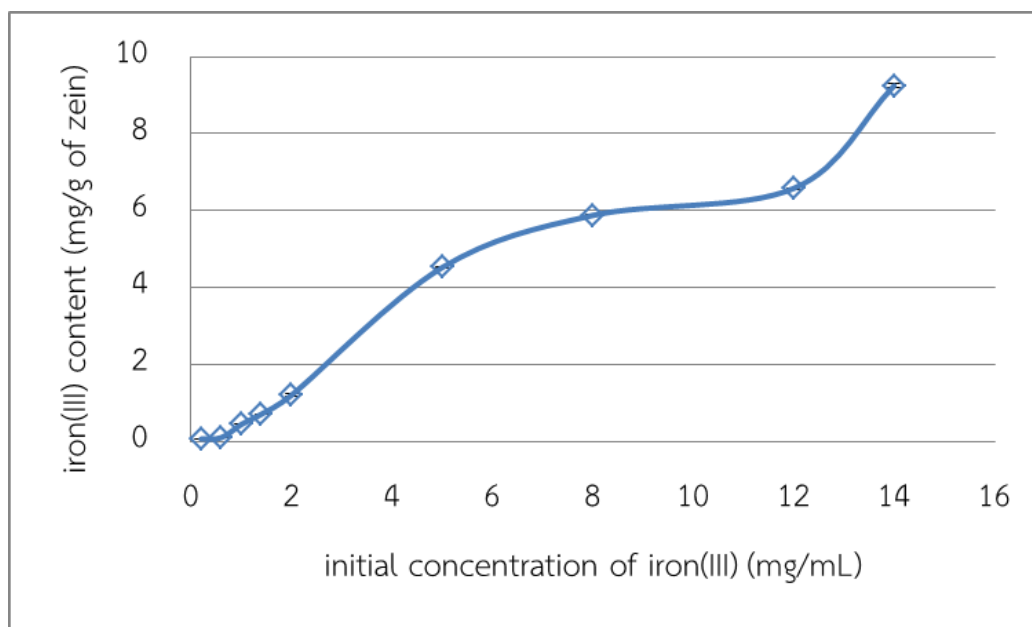


Figure 4.2 Iron content in the zein adsorbent determined by acid digestion/ICP-OES (n=3). Experimental conditions: adsorbent = 0.5 g, conc. HCl = 10 mL and digestion time 15 min.

Acid digestion was employed in the sample preparation for the determination of iron content in the adsorbent by ICP-OES method. Figure 4.2 revealed the iron content in the zein adsorbent as a function of the initial loading concentration of iron(III). The results show that the obtained iron content in the zein adsorbent increased proportionately with the concentration of FeCl_3 solution, therefore, it was literally confirmed that iron(III) from the FeCl_3 solution was successfully loaded into the adsorbent.

4.2.2 Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra in attenuated total reflectance (ATR) mode of the iron(III)-loaded zein-based adsorbent and THL-treated adsorbent at various temperatures are shown in Figure 4.3. The adsorbent spectra were compared with a blank spectrum of unmodified zein bead and collectively they were not significantly different. As a source of protein, zein bead clearly showed a spectrum (Figure 4.3(a)) with amide characteristic peaks of N-H stretching at 3290 cm^{-1} , N-H bending at 1636 cm^{-1} and C-H stretching around 2960 cm^{-1} . The spectrum of iron(III)-loaded adsorbent shown in Figure 4.3(b) was similar to that of zein bead, so FT-IR cannot be used to differentiate between these adsorbents. However, the spectra of THL-treated adsorbents (Figure 4.3(c-e)) are slightly different having a peak around $800 - 900\text{ cm}^{-1}$ that is referred to Fe-O-H bending of iron(III) oxide or iron(III) hydroxide formation [63]. Thus, it can be presumed that iron(III) in the adsorbents may have been converted into iron(III) oxide or iron(III) hydroxide by THL treatment process.

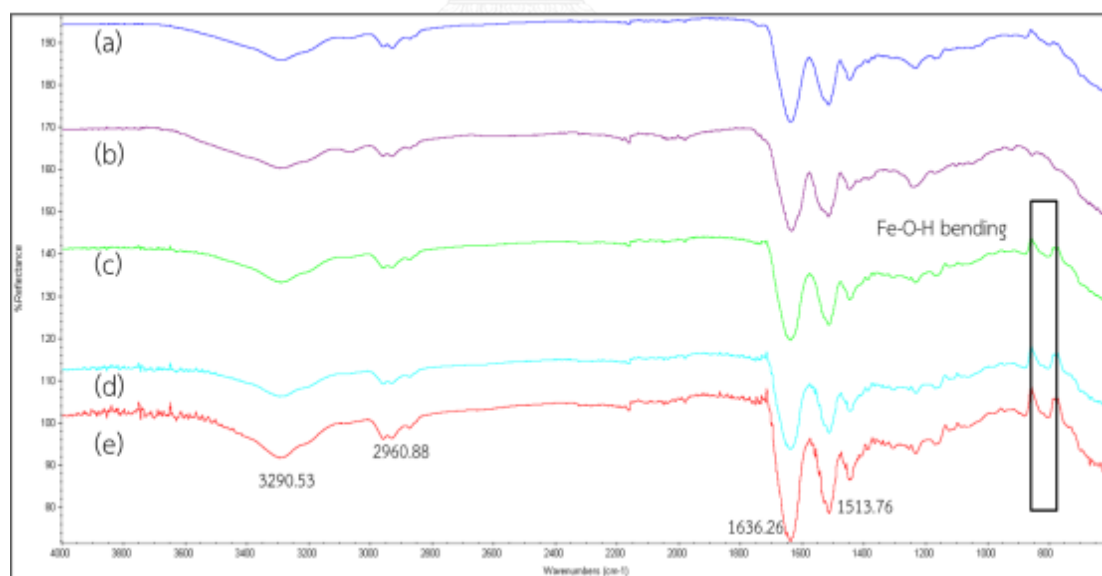


Figure 4.3 FT-IR spectra of (a) zein bead, (b) iron(III)-loaded zein-based adsorbent, (c-e) THL-treated adsorbent obtained at various temperatures of 60°C , 80°C and 100°C , respectively.

4.2.3 Scanning electron microscope with energy dispersive x-ray spectrometer (SEM-EDX).

In this work, the zein powder was transformed into beads, and the morphology of its surface was studied by SEM. The SEM image of zein bead is shown in Figure 4.4(a). The non-porous and slightly irregular surface of the zein bead was observed. The effect of iron(III) loading into the zein bead was investigated by adding a stock solution of the iron(III) solution in various concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, 2.5, 4.0, 6.0 and 7.0 mg/mL into the zein-based adsorbent. The SEM images of these adsorbents are shown in Figure 4.4(b-j). It was found that the addition of iron(III) to the adsorbent similarly change all of their morphology into substantially smoother surface. SEM-EDX was used to determine the amount of iron in the adsorbents; the SEM-EDX images were shown in Figure 4.5. The results (Table 4.1) showed that the elements mostly found in the adsorbent are carbon, nitrogen and oxygen because the zein-based adsorbent comprises of amino acid from protein. Iron (Fe) in the iron(III)-loaded adsorbent and THL-treated adsorbent were not observed by SEM-EDX technique probably because the amount or iron loaded into the adsorbent was below its detectability. Therefore, the x-ray fluorescence spectrometer was utilized for the determination of iron content in these adsorbents.

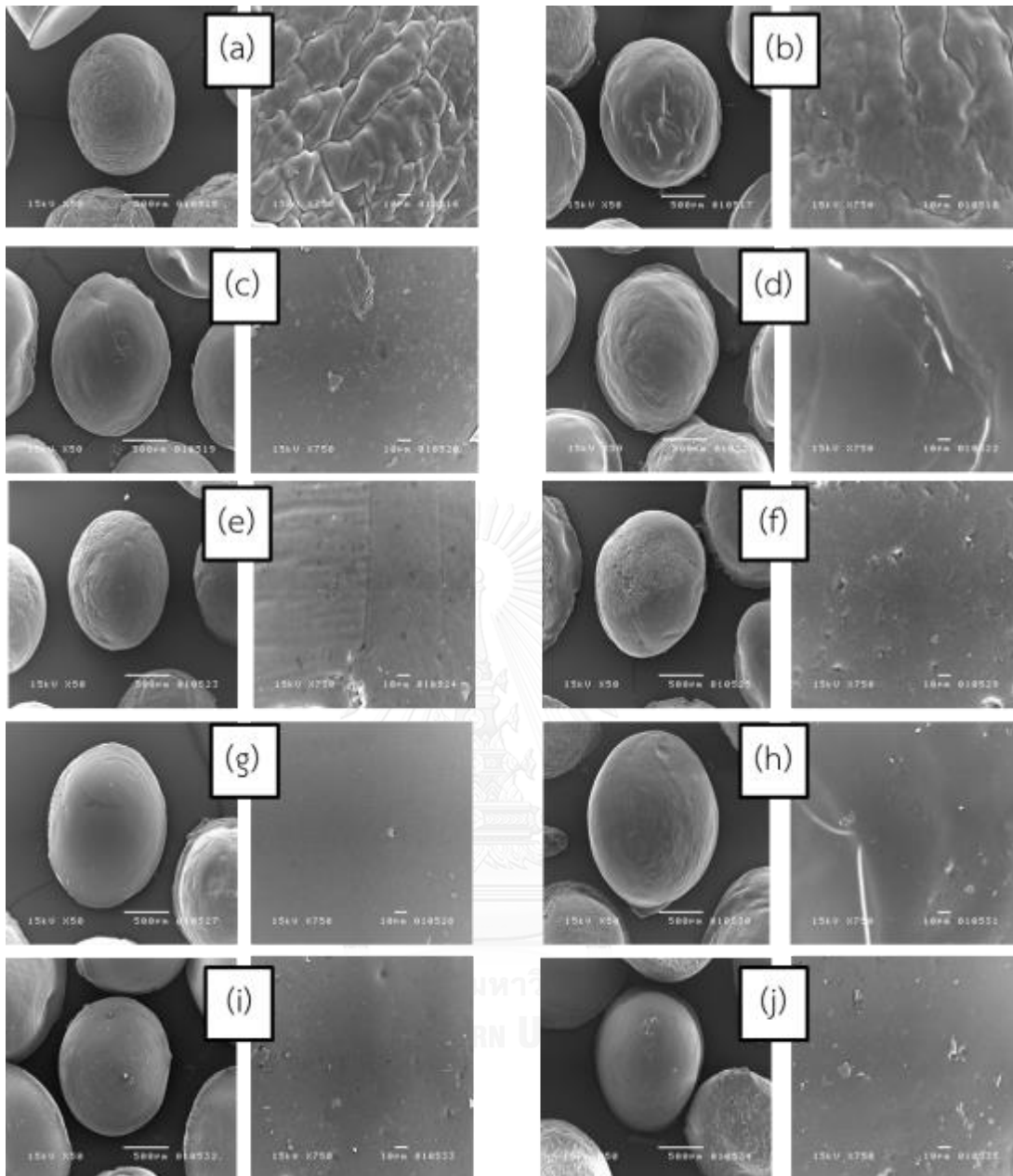


Figure 4.4 SEM images of (a) zein bead and (b-j) iron(III)-loaded zein based adsorbent in various concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, 2.5, 4.0, 6.0 and 7.0 mg/mL, respectively, under magnification of 50X (left image) and 750X (right image).

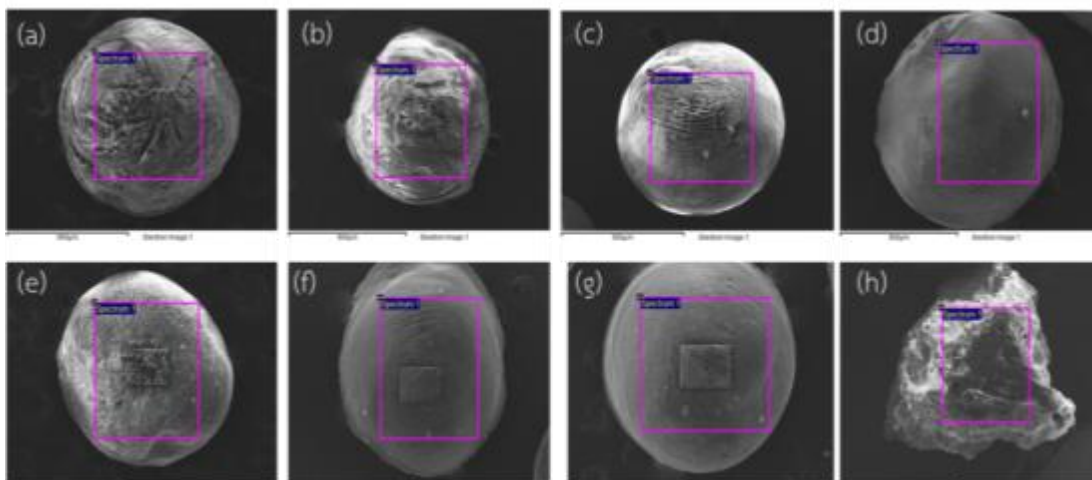


Figure 4.5 SEM-EDX images of (a) zein bead, (b-g) iron(III)-loaded in the concentration of 0.7, 1.0, 2.5, 4.0, 6.0, 7.0 mg/mL, respectively, and (h) THL-treated adsorbent.

Table 4.1 Element analysis of the adsorbents by SEM-EDX

Iron(III)-loaded (mg/mL)	C		N		O	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
0.0 (zein)	57.78	63.71	15.25	14.42	25.91	21.45
0.7	57.69	63.48	15.93	15.03	25.65	21.19
1.0	57.60	63.36	16.33	15.41	25.37	20.95
2.5	58.48	64.56	14.81	14.02	25.20	20.89
4.0	55.68	62.02	16.49	15.57	25.74	21.53
6.0	56.37	63.19	14.34	13.79	26.13	21.99
7.0	55.76	62.65	15.18	14.62	25.68	21.66
THL	48.90	54.66	21.39	20.50	29.47	24.72

4.2.4 X-ray fluorescence spectroscopy (XRF)

The amounts of iron contained in the adsorbents were determined by XRF method. The results are presented as weight percentages of Fe as shown in Table 4.2.

Table 4.2 XRF results showing amounts of iron (Fe) contained in the adsorbents loaded with various iron(III) concentrations

Iron(III)-loading concentration (mg/mL)	%Fe
0.0	0.0
0.1	1.84
0.3	3.63
0.5	4.14
0.7	7.93
1.0	9.41
2.5	5.82
4.0	5.21
6.0	5.40
7.0	5.45

It was found that the %Fe found in the adsorbents increased continually with the iron(III) loading concentrations up to approximately 1.0 mg/L. However, the additional amount of iron loading beyond this (2.5 – 7.0 mg/mL)

unexpectedly resulted in a loss of Fe incorporation into the adsorbent. The %Fe for these adsorbents were found relatively constant around 5% presumably because the excessive amount of FeCl_3 substantially decrease the pH of solution, as a result, Fe(III) could not formed and the retained on the adsorbent during the fabrication of the adsorbent beads

4.2.5 X-ray diffraction spectroscopy (XRD)

The XRD diffractograms of the unmodified zein bead and iron(III)-loaded zein based adsorbent are displayed in Figure 4.6. Both diffractograms did not show any crystalline peaks. Therefore, it can be presumed that these adsorbents were amorphous.

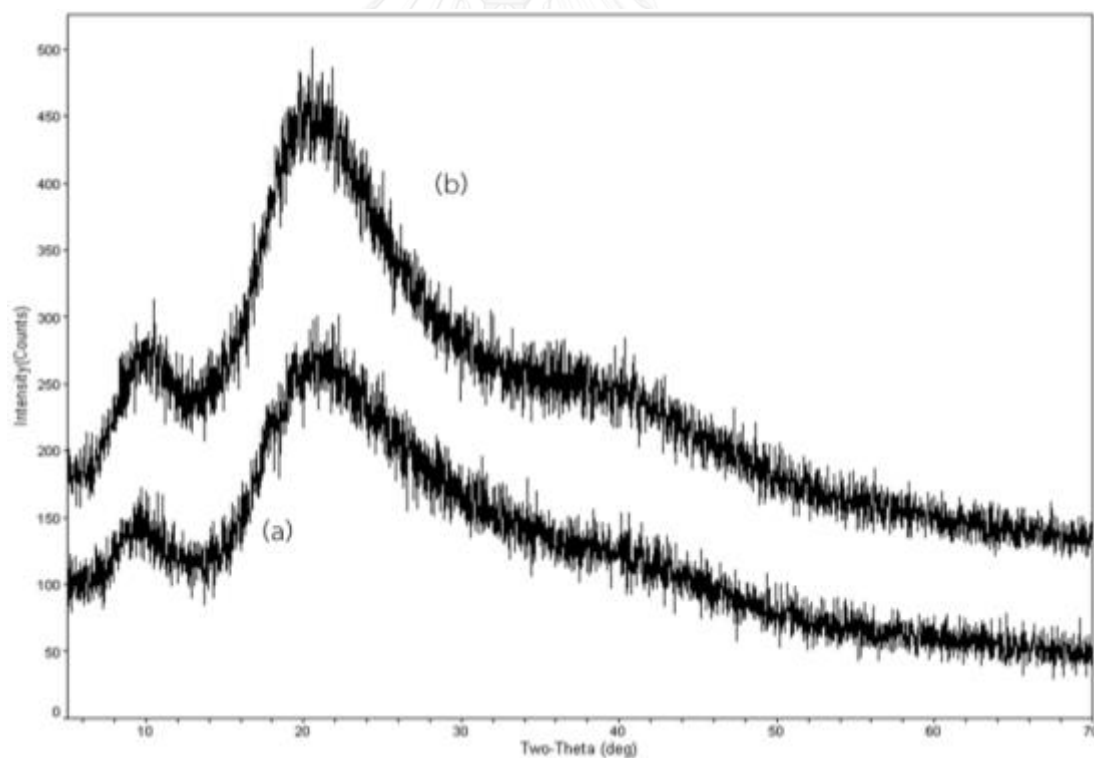


Figure 4.6 XRD patterns of (a) zein and (b) iron(III)-loaded zein bead adsorbent.

4.3 Adsorption of arsenic by iron(III)-loaded zein-based adsorbent

4.3.1 Effect of iron(III) concentration

The effect of initial iron(III) concentration for the preparation of adsorbent is an important parameter that should be examined and optimized in order to achieve the highest adsorption capacity. In this experiment, the initial iron(III) concentration was studied in the range of 0.1-7.0 mg/mL. The iron(III)-loaded adsorbents were investigated for arsenic removal with an adsorbent dose of 0.10 g, As(V) solution of 1.0 mg/L and a stirring speed of ~300 rpm for 2 hours at room temperature. The remaining concentrations of As(V) were determined by ICP-OES. The efficiency of arsenic removal against the concentrations of iron(III) loading is shown in Figure 4.7.

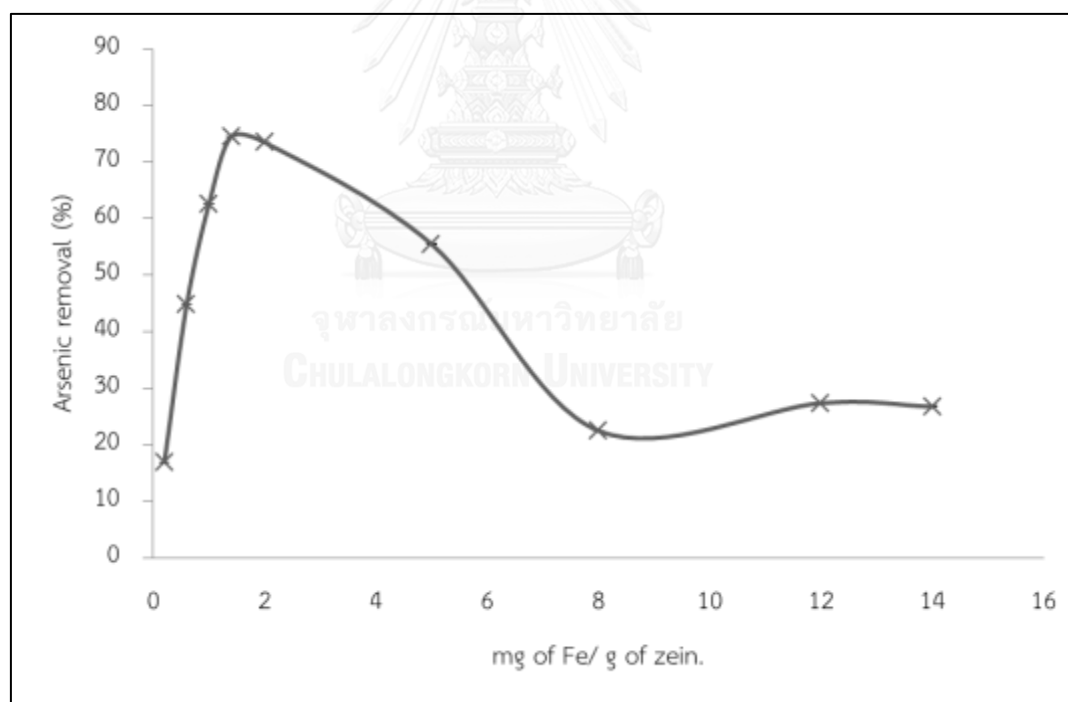
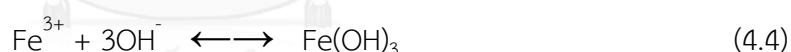
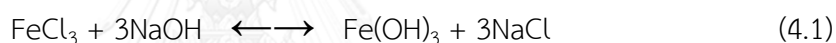


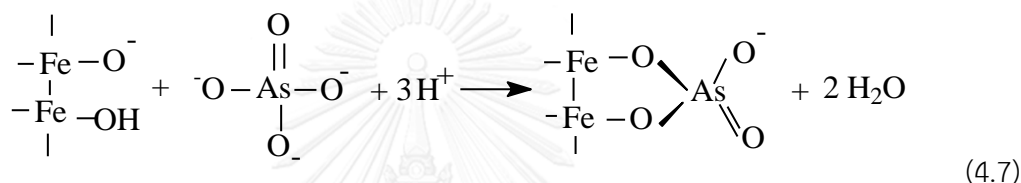
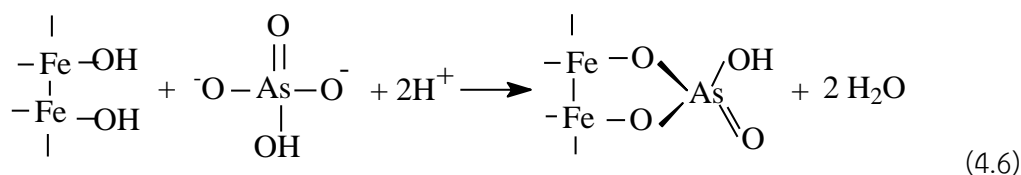
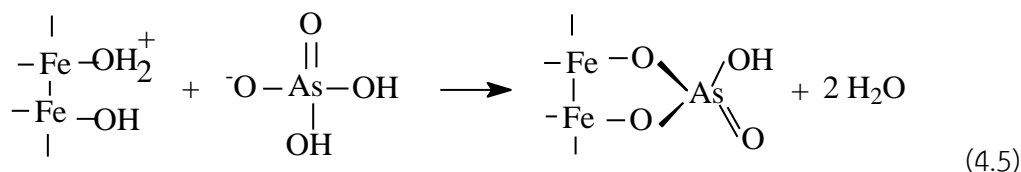
Figure 4.7 Effect of iron(III) loading concentrations on the removal of arsenic(V) (n=3). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, volume = 10 mL, adsorbent = 0.1 g and adsorption time = 2 h.

The results indicated that increasing the initial iron(III) loading concentration in the range of 0.2 – 1.0 mg of Fe/g of zein continually yielded increasing percentages of arsenic removal. The highest arsenic adsorption efficiency was achieved by using 0.7 mg/mL of iron(III)-loaded concentration (1.4 mg of Fe/ g of zein). Nevertheless, with higher iron(III) concentration, i.e. above 0.7 mg/mL (8 mg of Fe/g of zein), the percentage of arsenic removal significantly dropped from 80% to around 30% These findings conformed well with the amount of Fe found on the adsorbent surface (Table 4.2) affirming the interaction between the two species.

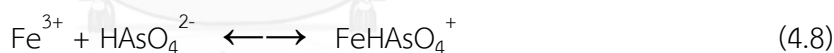
The iron on the adsorbent surface could be present in various forms such as iron oxide and/or iron hydroxide (iron hydroxide) and free iron(III) depending on the concentration of sodium hydroxide solution that was added in the adsorbent preparation process. Therefore, the possible forms of iron in the adsorbent are shown below;



Therefore, arsenic was likely adsorbed by complexation between iron(III) and HAsO_4^{2-} , or by electrostatic interaction of the arsenate and Fe(OH)_3 [64]. The mechanism of arsenic(V) adsorbed onto this adsorbent was described by reactions of iron hydroxide on the adsorbent bead. The adsorption reactions of arsenic(V) on iron hydroxide by bidentated-binuclear complex in acidic condition, near neutral condition and basic condition were proposed in Equation 4.5, 4.6 and 4.7, respectively [55].



The presence of iron(III) in the adsorbent and HAsO_4^{2-} (at pH 6) could interact and form iron arsenate complex as shown in Equation 4.8 [64].



With higher concentration of iron(III), the adsorption substantially decreased possibly due to unfavorable condition. As iron(III) was added as FeCl_3 , the solution became more acidic at higher concentrations and as a result, $\text{Fe}(\text{OH})_3$ could not be formed under this condition (Figure 4.8). In addition, at this acidic condition, iron(III) in the iron(III)-loaded zein solution can be released during bead formation in the water media as well. However, a basic condition by the addition of excess NaOH is not suitable for the synthesis of the adsorbent because the iron(III)-loaded zein solution would be too viscous that it could not be filled in a syringe and dropped to produce beads. It was found that the zein-based adsorbent loaded with 0.7 mg/mL of iron(III) solution provided the highest percentage of the arsenic removal, so this loading concentration was chosen for further experiments.

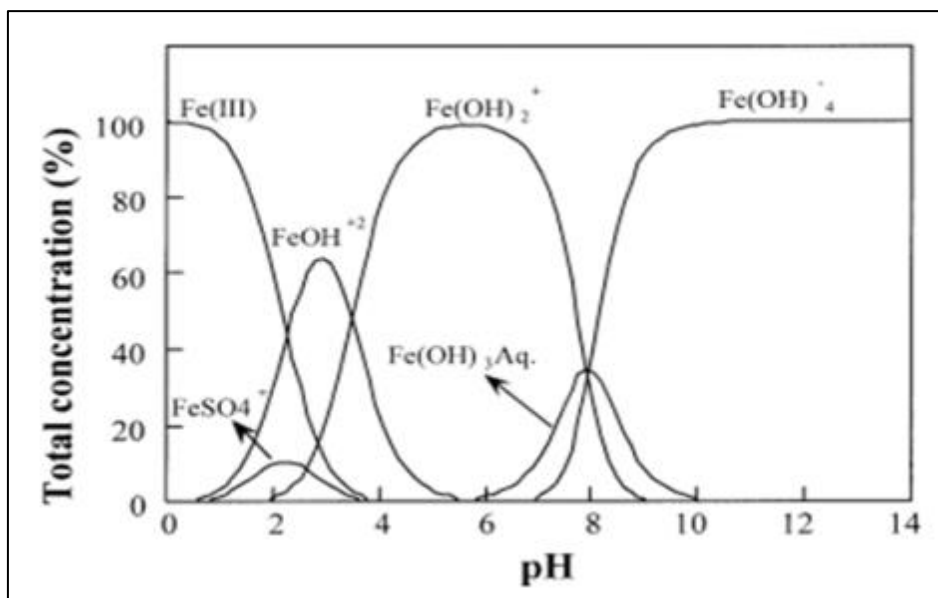


Figure 4.8 Distribution diagram of iron(III) species at different pH values [65].

4.3.2 Effect of pH

The pH of solution can greatly affect the distribution of arsenic species as mentioned previously. This work was therefore conducted to investigate the effect of pH on the arsenic removal from pH 3-9. A 0.10 g iron(III)-loaded zein-based adsorbent was mixed with a solution containing 1.0 mg/L arsenic at the desired pH, and then the solution was stirred at 300 rpm for 2 hours at room temperature. The effect of pH values from 3-9 toward arsenic removal is illustrated in Figure 4.9. Because arsenic normally exists as oxyanion; $\text{H}_2\text{AsO}_4^{2-}$ and HAsO_4^- , that are negatively charged under pH 3-9, they were effectively interacted with iron(III) by electrostatic force and adsorbed. In addition, it was shown that the solutions at pH 3 and 6 provided slightly higher percentages of the arsenic removal (about 80%). According to the distribution diagram in Figure 4.8, the FeOH^{2+} and Fe(OH)_2^+ species are predominant at pH 3 and 6, respectively, thereby promoting the arsenic adsorption efficiency under these conditions. This in turn makes the technique somewhat beneficial toward its application as adsorbent for a variety of samples and wastewater with minimum pH adjustment, i.e. pH 3 can be used for acidic wastes. For the case of study, pH 6 was chosen as optimal for further experiments.

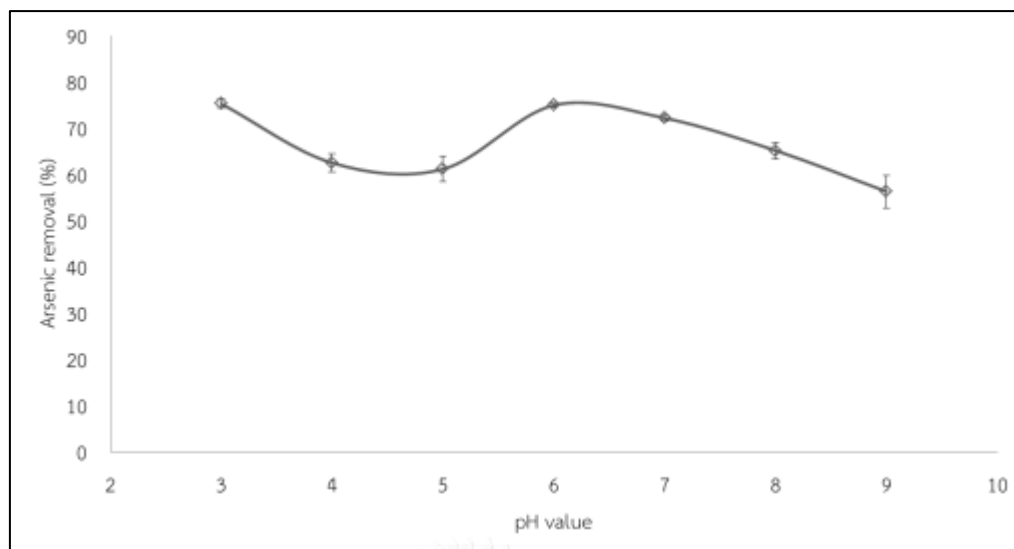


Figure 4.9 Effect of pH of the solution on As(V) removal (n=3). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g and adsorption time = 2 h.

4.3.3 Effect of adsorption time

The adsorption time is one of the key parameters for an adsorption process. A 10 mL of an 1.0 mg/L arsenic solution was adjusted to be pH 6 and mixed with 0.10 g of iron(III)-loaded zein based adsorbent under stirring speed of 300 rpm at room temperature for various adsorption times of 15, 30, 60, 120, 240, 480 and 960 minutes. The effect of adsorption time on the arsenic removal is shown in Figure 4.10. It was found that increasing the adsorption time produced progressively higher adsorption efficiency until it apparently reach the equilibrium after 8 hours obtaining over 90% of arsenic removal. However, the absorption time of 16 hours is more convenient for a practical use as this step is normally carried out overnight.

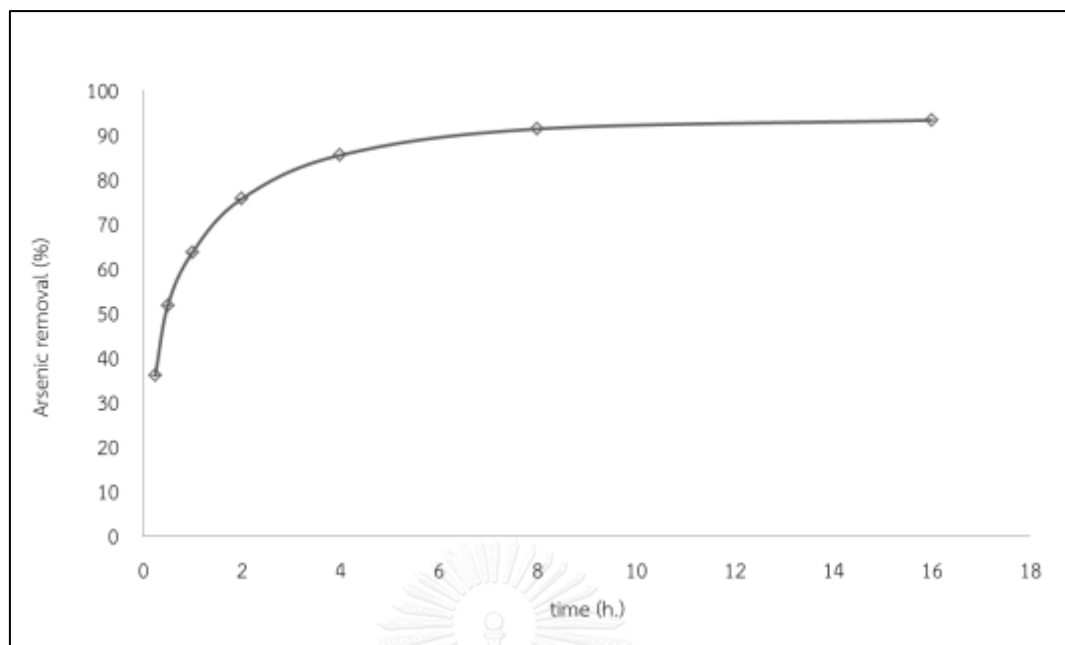


Figure 4.10 Effect of adsorption time on the As(V) removal (n=3). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g and pH =6.

4.3.4 Adsorption isotherm

Under the optimal condition, the adsorption isotherm was conducted to investigate the adsorption phenomena of arsenic. A 0.10 g of the synthesized adsorbent was mixed with a pH 6 solution containing As(V) in various concentrations, i.e. 0.5, 1, 10, 30, 50, 70 and 100 mg/L, respectively. The adsorbent was allowed to remove As(V) from the solution for 16 hours at room temperature. The remaining As(V) concentrations were determined by ICP-OES. The relationship between the adsorption capacity (mg/g) and the initial arsenic concentration (mg/L) is shown in Figure 4.11. The results presented that the adsorption capacity of adsorbent rapidly increased at C_e of 0.5 – 40 mg/L and then slightly increased to a limited value at C_e higher than 50 mg/L.

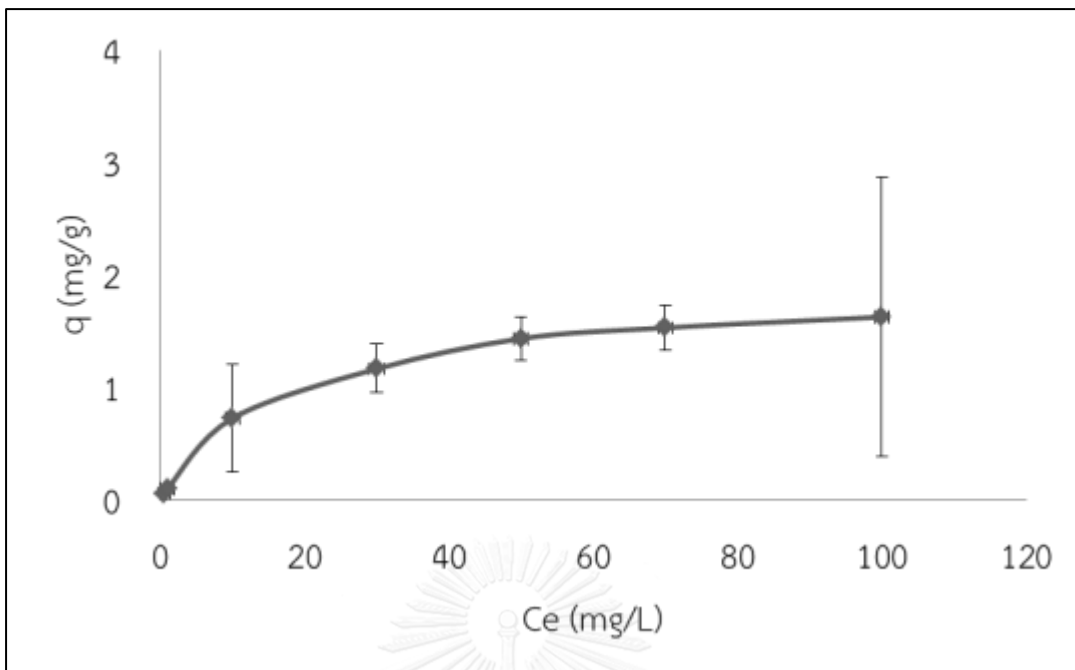


Figure 4.11 Arsenic adsorption capacity of the adsorbent as a function of initial concentration of As(V) ($n=3$). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g, pH =6 and adsorption time 16 h.

The adsorption behavior of As(V) on the adsorbent was described by two general models; the Langmuir and the Freundlich adsorption isotherms. The Langmuir adsorption isotherm was derived from a plot between C_e/q and C_e from Equation 2.2 as shown in Figure 4.12, while the Freundlich adsorption isotherm was plotted between $\log q$ and $\log C_e$ from Equation 2.3 as shown in Figure 4.13.

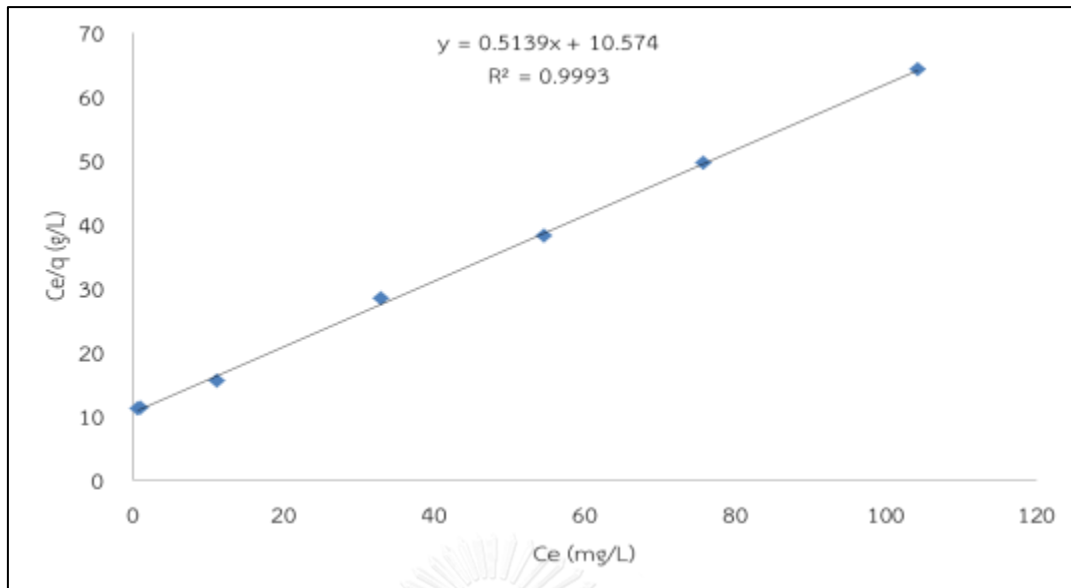


Figure 4.12 Langmuir adsorption isotherm plot of arsenic adsorption.

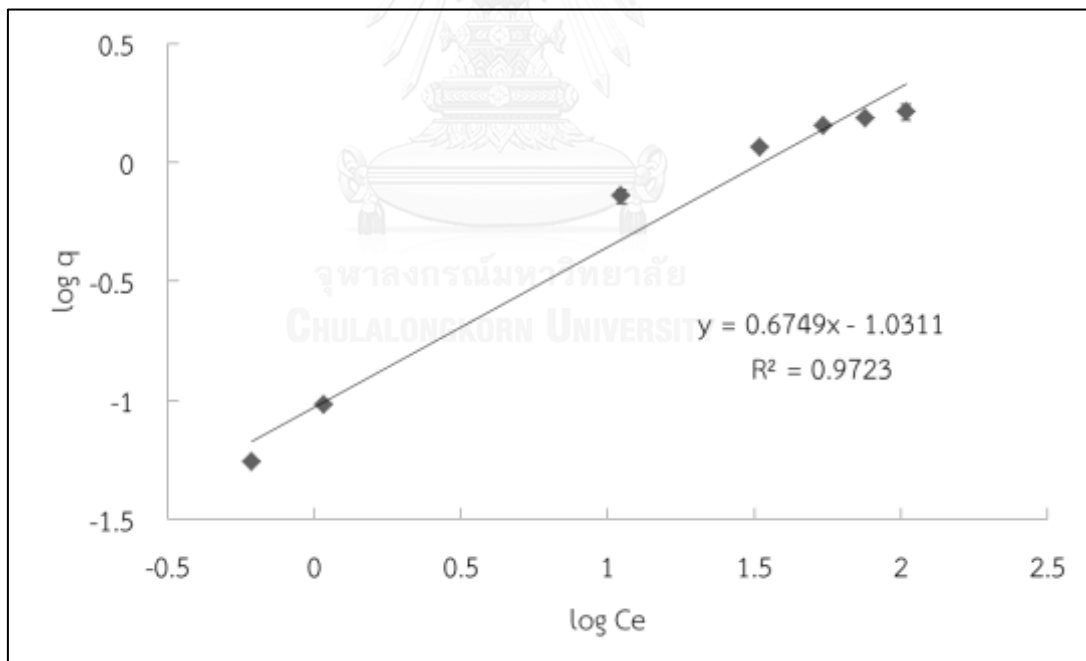


Figure 4.13 Freundlich adsorption isotherm plot of arsenic adsorption.

The Langmuir adsorption isotherm is a model which describes the interaction between the active site of adsorbent and the adsorbed molecule as a monolayer on the homogeneous surface of adsorbent. In contrast, the Freundlich adsorption isotherm allows the formation of multilayer of adsorbed molecules on the heterogeneous surface.

The correlation coefficient (R^2) of the curve fitting to each model is used to determine the adsorption phenomenon of the adsorbent. The results showed that the Langmuir plot produced a linear regression plot with R^2 of 0.9993 while the Freundlich plot showed R^2 of 0.9723. This experiment was better fitted with Langmuir adsorption isotherm and thus it was concluded that this adsorption process is a monolayer adsorption with the maximum adsorption capacity 1.95 of mg/g and the constant related to the free energy of 0.05 L/mg.

4.3.5 Interference study

Anions commonly found in natural water are phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), carbonate (CO_3^{2-}), chloride (Cl^-) and nitrate (NO_3^-). This experiment was designed to study the interference of these ions against the removal of arsenic oxyanions. Each interfering ion at various concentrations of 1, 10 and 100 mg/L was added into 1 mg/L of arsenic solution as binary mixtures. The mixtures were then subject to the arsenic removal using 0.1 g of adsorbent at pH 6. Each mixture was stirred (~300 rpm) at room temperature for 16 hours. After that, they were analyzed for the remaining As(V) concentrations by ICP-OES.

Figure 4.14 showed that the higher concentrations of interference ions, especially, PO_4^{3-} , CO_3^{2-} and SO_4^{2-} , caused significant decreases of arsenic removal efficiency probably because these ions are more negatively charged than those of arsenate which is present as H_2AsO_4^- at pH 6 (optimum pH). A larger suppression of arsenic removal was particularly noted for phosphate as compared to sulphate and carbonate presumably as a result of its more negatively charged structure. Based on

these results, these three ions, probably along with other similar anions, must be removed or masked in order to maximize the arsenic removal efficiency.

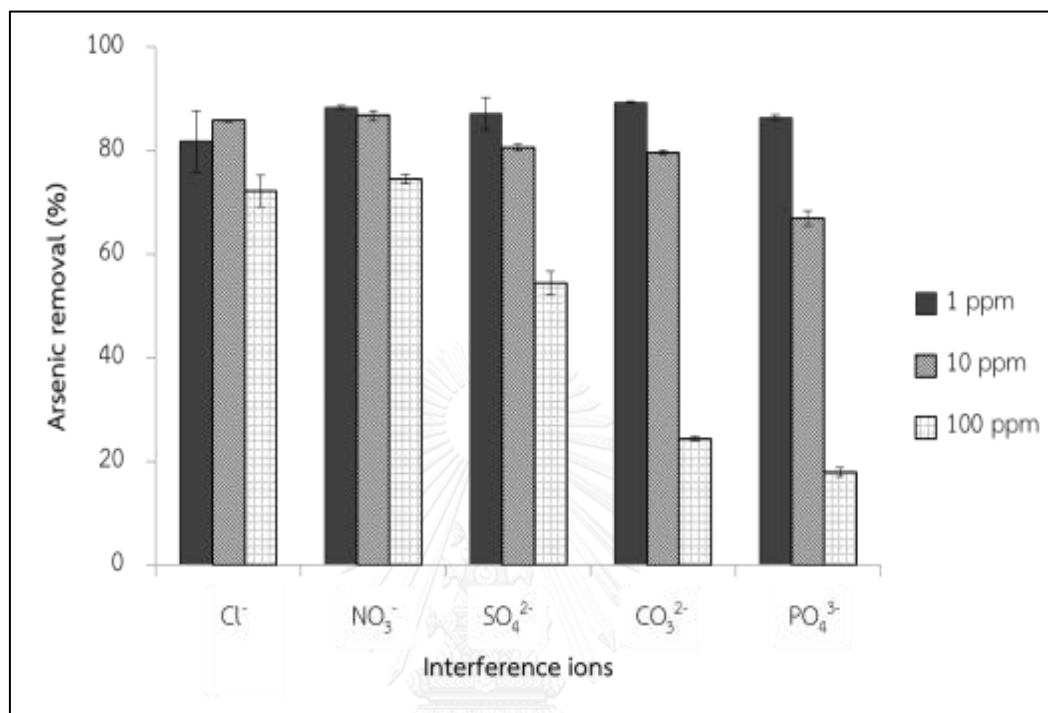


Figure 4.14 Efficiency of the arsenic removal interfered by common anions at various concentration of 1, 10, 100 mg/L (n=3). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g, pH =6 and adsorption time 16 h.

4.4 Adsorption of arsenic(III) by iron(III)-loaded zein-based adsorbent

The optimal conditions obtained for the As(V) removal were adopted for the investigation of As(III) removal. However, as mentioned above, arsenic can be present in different species depending on the pH value and so the effect of pH was re-optimized in the range of pH 3-10 for the As(III) adsorption. A 0.10 g of synthesized adsorbent and a 10 mL of 1 mg/L As(III) solution were mixed and stirred with 300 rpm speed at room temperature. After stirring for 16 hours, the remaining

As(III) concentration was determined by ICP-OES. The adsorption profile was illustrated in Figure 4.15.

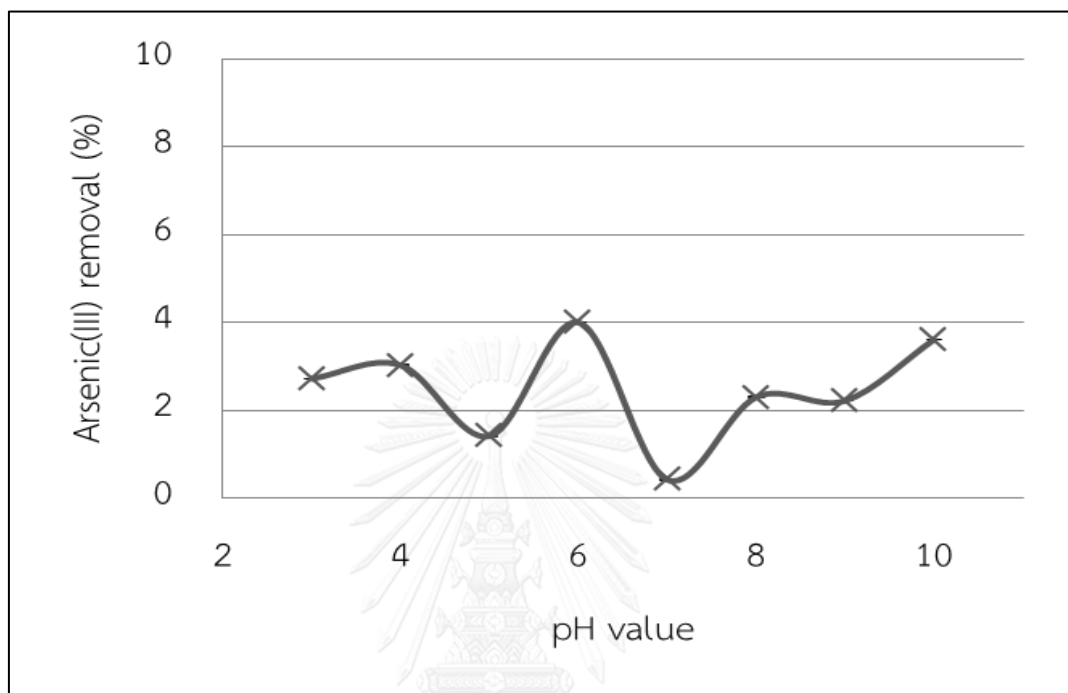


Figure 4.15 Adsorption profile of the As(III) removal under the different pH values (n=3). Experimental conditions: initial arsenic(III) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g and adsorption time 16 h.

It was clearly seen that only a few of As(III) can be removed from the solutions under the pH range of 3-10 by the iron(III)-loaded zein-based adsorbent. Because As(III) is present as H_3AsO_3 (non-charged form) under the pH range of 1-8 as shown in Figure 2.2(b), its interaction with Fe(III) in the adsorbent was unfavorable. At pH 9-10, As(III) is in the form of H_2AsO_3^- while Fe(III) exists as $\text{Fe}(\text{OH})_4^-$ (Figure 4.8), both of which are negatively charged and are likely subject to the electrostatic repulsion making the arsenic adsorption nearly impossible.

4.5 Adsorption of arsenic by thermal hydrolysis-treated adsorbent

4.5.1 Effect of temperature for THL

The synthesized adsorbent was modified by THL technique in order to improve its adsorption capacity. The efficiency of arsenic removal via the THL-treated adsorbent at various temperatures of 60, 80 and 100°C compared to those using untreated adsorbent are shown in Figure 4.16. It was found that the adsorbents treated with THL at the studied temperatures provided about 50% lower efficiency of arsenic removal compared with using the non-treated adsorbent. In particular, the efficiency of As(V) removal decreased when the THL treated temperature increased. This can be explained by two reasons with the first being that zein protein, a major component of the adsorbent, was apparently denatured under higher temperature. The other reason is that iron(III) might be released to the media solution because some of the interaction between iron(III), which is classified to be a hard Lewis acid by the Hard-Soft Acid-Base principle (HSAB), and amine functional group (R-NH₂) of zein which is a hard Lewis base, was broken by the energy attained at high temperatures.

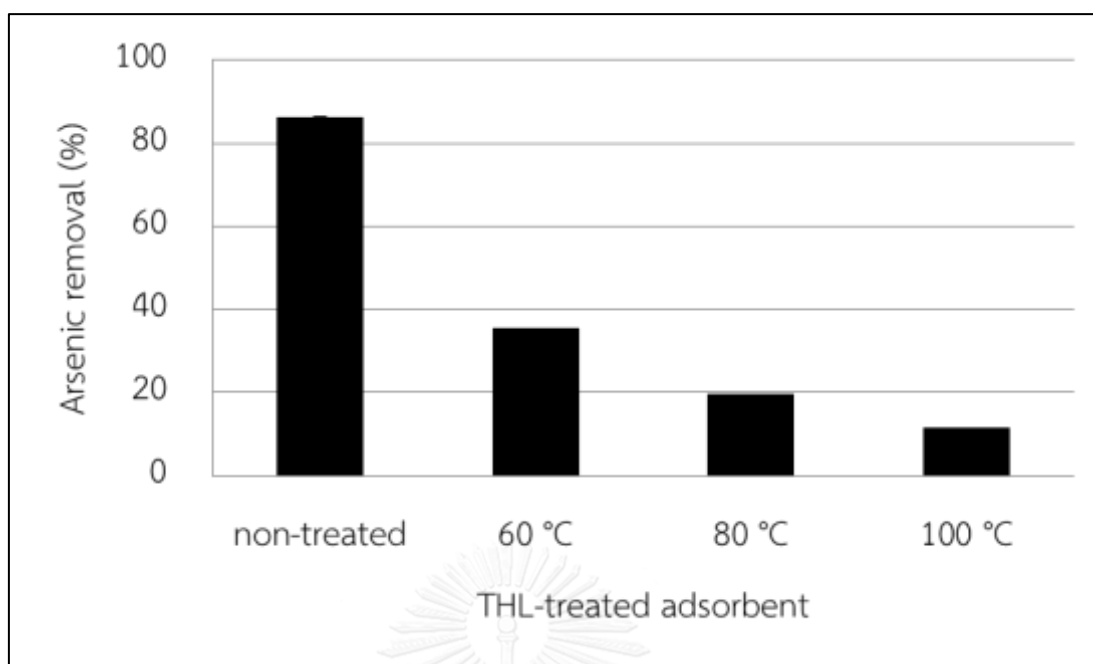


Figure 4.16 Arsenic adsorption efficiency of adsorbents treated with THL at various temperatures of 60, 80 and 100 °C compared to the non-treated adsorbent (n=3). Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g, pH =6 and adsorption time 16 h.

4.5.2 Characterization of THL-treated adsorbent

To rationalise the observation from the previous experiment, the amount of iron(III) content in the THL-treated adsorbents were determined. The solutions from the digestion of adsorbents treated with THL at the temperatures of 60, 80 and 100 °C were filtered and analyzed by ICP-OES. Their results are presented in Figure 4.17. When the heating temperature increased, the arsenic adsorption efficiency of THL-treated adsorbent decreased whereas iron concentration in the media increased (see Figure 4.17). From this result, it can be concluded that the THL process can lead to the dissociation of the bonding between iron(III) and amine in the adsorbent, thus these high temperatures can result in the release of iron(III) from the adsorbent surface and adversely affect the arsenic adsorption efficiency. This

assumption was well supported by the result of total iron content in the THL-treated adsorbents that were determined by acid digestion as shown in Figure 4.18. Iron in the adsorbent was presumably repelled from the bead into the media via thermal hydrolysis treatment and thus it was not an appropriate means to improve these adsorbents.

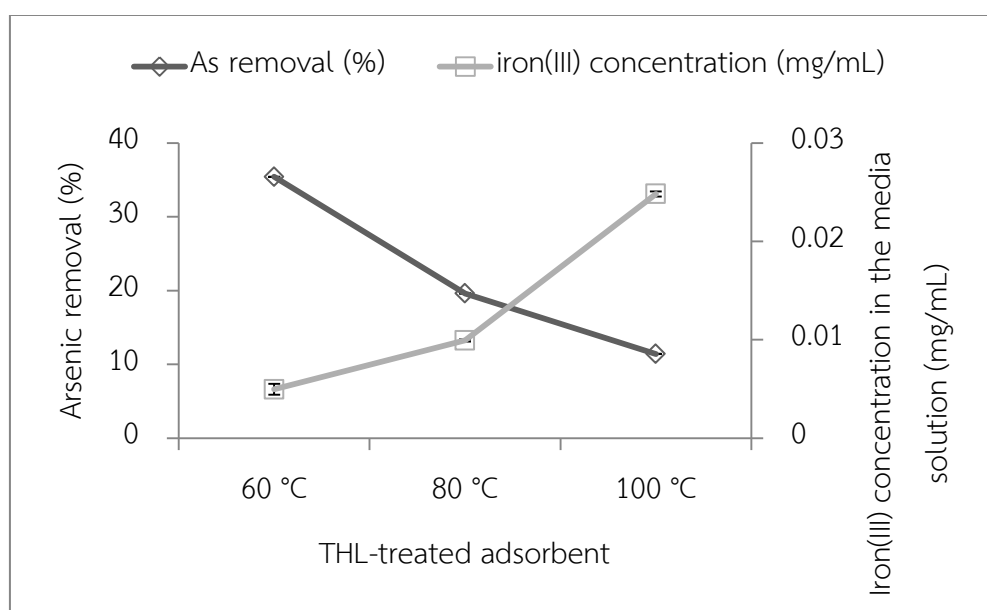


Figure 4.17 Effect of the used THL temperatures on the amount of iron(III) in the THL-treated adsorbent and the arsenic adsorption efficiency (n=3).

Experimental conditions: initial arsenic(V) concentration = 1.0 mg/L, initial iron(III) concentration = 0.7 mg/mL, volume = 10 mL, adsorbent = 0.1 g, pH = 6 and adsorption time 16 h.

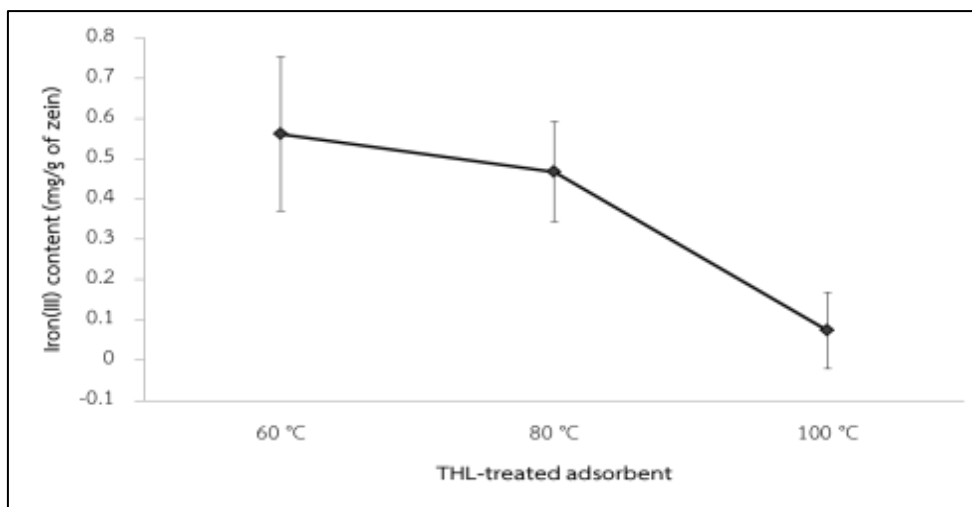


Figure 4.18 Iron content in the THL-treated adsorbent determined by acid digestion/ICP-OES (n=3). Experimental conditions: adsorbent = 0.1 g, conc. HCl = 5 mL and digestion time 15 min.

4.6 Arsenic removal from real water samples

The arsenic removal by the synthesized adsorbent of two industrial wastewater samples, TK-80 and TK-81, were investigated. Since, the adsorbent can only effectively remove As(V), the samples were thereby oxidized by excess KMnO_4 to convert As(III) to As(V) and then adjusted to pH 6. Under the optimized conditions of the adsorption, the efficiencies of arsenic removal of the samples were determined.

Table 4.3 The arsenic removal from the wastewater samples (TK-80 and TK-81).

Sample	Arsenic removal (%)	
	Non-oxidized	Oxidized (pH6)
TK-80	15.2 ± 1.0	43.3 ± 0.5
TK-81	8.6 ± 0.5	46.2 ± 0.3

From Table 4.3, the percentages of arsenic removal increased significantly after the pretreatment with the oxidation process. The efficiency of arsenic removal was improved from 15 % to 43% and 8% to 46% for TK-80 and TK-81, respectively, indicating that the majority of arsenic in these samples are originally present as As(III). The efficiency of As(V) removal in TK-80 and TK-81 were not ideal probably as a result of interference ions normally present in such samples.

A natural water sample represented by Chulalongkorn University's pond water and three drinking water samples from different manufacturers were additionally used for the assessment of arsenic removal efficiency of the developed adsorbent. As no arsenic was found in any of these samples, a spike of 1.0 mg/L As(V) was added to all samples. The adsorbent was allowed to adsorb As(V) under the optimal conditions and the remaining arsenic concentration was determined. The results are summarized in Table 4.4. It was found that the arsenic removal from the spiked drinking water I sample exhibited the highest adsorption efficiency of 92.5 %, while the efficiencies of the drinking water II and III were lower. These latter two samples are mineral water that normally contain relatively high level of mineral ions, some of which evidently can interfere or compete with the adsorption of As. The largest suppression of arsenic removal for drinking water III was due to the high concentration of total dissolved solids and total hardness contained in this sample. Hence, it was suggested that arsenic adsorption by the iron(III)-loaded zein based adsorbent was best achieved when the samples contain no or masked of interference ions.

Table 4.4 The arsenic removal of spiked water samples.

Water sample	Arsenic removal (%) (n=3)
Pond water	43.51 ± 0.06
Drinking water I	92.49 ± 0.00
Drinking water II (mineral water)	73.72 ± 0.01
Drinking water III (mineral water)	20.57 ± 0.02



CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

The iron(III)-loaded zein based adsorbent that demonstrated a promising capability as an effective low-cost adsorbent for arsenic removal was developed. This adsorbent was simply prepared by dissolving zein powder, mixing with ferric chloride, dropping into the cold water to form beads, and then drying overnight at room temperature. The synthesized adsorbent was characterized by scanning electron microscope (SEM), X-ray fluorescence spectrometer (XRF) and inductively coupled plasma-optical emission spectrometer (ICP-OES). The adsorbent was amorphous and comprised mainly of carbon, nitrogen, oxygen and iron in proportion with the iron loading amount.

Various parameters were investigated for the arsenic adsorption, for example, the amount of iron(III) loaded in the synthesis adsorbent process, the pH value of solution and the adsorption time. All of the experiments were performed at room temperature. The results showed that the optimal iron(III) loading concentration was 0.7 mg/mL FeCl₃, the optimum pH solution for the removal of arsenic was pH 6, and the appropriate adsorption time was 8 hours or longer. The adsorption of arsenic by this adsorbent followed Langmuir adsorption isotherm with R² of 0.9993 with the maximum adsorption capacity of 1.95 mg/g. Furthermore, the interference studies found that two anions commonly found in the water sample, namely sulphate, carbonate and phosphate, significantly affected the capability of arsenic removal. The thermal hydrolysis technique was used unsuccessfully to improve the efficiency of arsenic adsorption even though the higher incorporation of Fe into the adsorbent was attained, presumably as a result of loss of Fe from the adsorbent surface by heat treatment.

In addition, the synthesized adsorbent was applied to arsenic(V) removal in real water samples with oxidation pretreatment and pH adjustment prior to the

adsorption. The arsenic removal from real water samples, TK-80 and TK-81, were 43.25 and 46.16%, respectively. This somewhat less-than-ideal removal efficiency was probably caused by the interference ions in the sample competing with arsenic in the adsorption process as a much higher removal efficiency (>90%) was obtained with a clean drinking water I sample. Meanwhile, drinking water II and III samples which are mineral water, that contain a lot of interfering ions yielded poorer results. It was therefore suggested that the synthesized adsorbent performed more effectively toward arsenic removal in the interference free samples and common ions should be removed or masked off prior to the adsorption.

5.2 Suggestion for future work

- To enhance the arsenic adsorption capacity, sulphate and phosphate should be eliminated from water samples by masking agent or by pre-treatment with some removal method.
- The iron(III)-loaded zein-based adsorbent should be applied as low-cost adsorbent for column system to remove arsenic in water sample.
- The regeneration process of the adsorbent should be developed.

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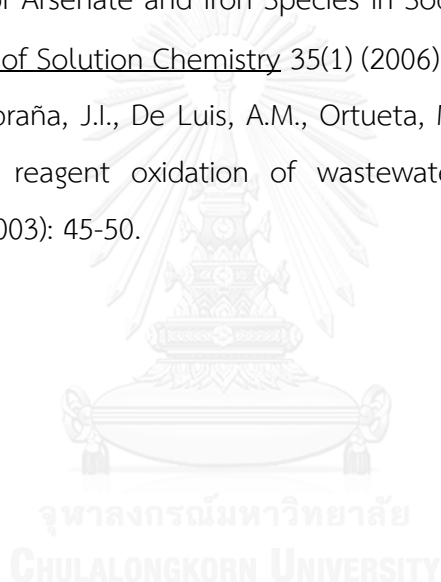
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