การขจัดอาร์เซนิกจากน้ำเสียโดยการตกตะกอนร่วมด้วยเฟอร์ริกไอออนและสารส้มโดยใช้วิธีการออกแบบการทดลอง

นายอิสริยะ วิทยารักษ์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

REMOVAL OF ARSENIC FROM WASTEWATER BY CO-PRECIPITATION WITH FERRIC IONS AND ALUM USING EXPERIMENTAL DESIGN APPROACH

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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
Chulalongkorn University
Academic Year 2014

Thesis Title	REMOVAL OF ARSENIC FROM WASTEWATER BY CO-PRECIPITATION WITH FERRIC IONS AND ALUM USING EXPERIMENTAL DESIGN APPROACH
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อิสริยะ วิทยารักษ์ : การขจัดอาร์เซนิกจากน้ำเสียโดยการตกตะกอนร่วมด้วยเฟอร์ริกไอออนและสารส้มโดยใช้วิธีการออกแบบการทดลอง (REMOVAL OF ARSENIC FROM WASTEWATER BY CO-PRECIPITATION WITH FERRIC IONS AND ALUM USING EXPERIMENTAL DESIGN APPROACH) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.อภิชาติ อิ่มยิ้ม, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร.คเณศ วงษ์ระวี, 89 หน้า.

การออกแบบการทดลองโดยใช้วิธี Full Factorial Design (FFD) และ Central Composite Design (CCD) และ เทคนิค Response Surface Methodology (RMS) เพื่อหาภาวะที่เหมาะสมสำหรับขจัดอาร์เซไนต์และอาร์เซเนตด้วยวิธีตกตะกอนร่วมโดยใช้เฟอร์ริกคลอไรด์และสารส้มเป็นตัวตกตะกอนร่วม รวมทั้งศึกษาปัจจัยที่มีผลต่อการตกตะกอนของตัวแปรต้นและความสัมพันธ์ของตัวแปรต้นที่มีต่อกัน เมื่อใช้วิธี FFD พบว่าการขจัดอาร์เซไนต์และอาร์เซเนตที่ความเข้มข้นเท่ากับ 90 มิลลิกรัมต่อลิตร มีประสิทธิภาพสูงสุดเมื่อ พีเอชเท่ากับ 7 ความเข้มข้นเฟอร์ริกไอออนเท่ากับ 225 มิลลิกรัมต่อลิตร และความเข้มข้นของอะลูมิเนียมไอออนเท่ากับ 135 มิลลิกรัมต่อลิตร นอกจากนี้ สำหรับการออกแบบการทดลองโดยใช้วิธี CCD ศึกษาตัวแปรต้นและความสัมพันธ์ของตัวแปรต้นที่มีต่อกัน ได้แก่ พีเอช ปริมาณตัวตกตะกอนร่วม และปริมาณอาร์เซนิกเริ่มต้น ที่มีผลต่อการตกตะกอนอาร์เซนิก โดยตัวแปรดังกล่าวถูกศึกษาในฟังก์ชันถดถอย (regression function) โดยใช้วิธี Multiple Linear Regression (MLR) และใช้วิธีการทางสถิติแบบ Analysis of Variance (ANOVA) เพื่อศึกษาระดับความสำคัญของตัวแปรต่าง ๆ โดยศึกษาจากค่า *p*-values <0.01 ผลปรากฏว่าตัวแปรต้นทั้งสามมีความสำคัญต่อการตกตะกอนอาร์เซนิก และค่าสัมประสิทธิ์ความถูกต้อง (R^2) ระหว่างผลการทดลองกับผลจากการทำนายประสิทธิภาพการขจัดอาร์เซไนต์และอาร์เซเนตในสมการถดถอย เมื่อใช้เฟอร์ริกคลอไรด์เท่ากับ 0.9871 และ 0.9478 ตามลำดับ สำหรับประสิทธิภาพการขจัดอาร์เซนิกสูงสุดได้เกือบ 100 % ที่ภาวะความเข้มข้นของเฟอร์ริกไอออนเท่ากับ 225 มิลลิกรัมต่อลิตร และพีเอช 7 ใช้ภาวะที่ได้นี้ในการขจัดอาร์เซนิกในตัวอย่างน้ำเสียจากโรงงาน 2 ตัวอย่าง ได้ประสิทธิภาพเท่ากับ 93.98 และ 91.48% ซึ่งสามารถยืนยันได้ว่าวิธีตกตะกอนร่วมพร้อมกับใช้การออกแบบการทดลองเพื่อหาภาวะที่เหมาะสม สามารถขจัดอาร์เซนิกในน้ำเสียตัวอย่างได้จริง

ภาควิชา	เคมี	ลายมือชื่อนิสิต	....
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5572238823 : MAJOR CHEMISTRY

KEYWORDS:

ITSARIYA WITTAYARAK: REMOVAL OF ARSENIC FROM WASTEWATER BY CO-PRECIPITATION WITH FERRIC IONS AND ALUM USING EXPERIMENTAL DESIGN APPROACH. ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., CO-ADVISOR: ASST. PROF. KANET WONGRAVEE, Ph.D., 89 pp.

Full Factorial Design (FFD) and Central Composite Design (CCD) with Response Surface Methodology (RSM) are applied to evaluate optimized conditions for As(III) and As(V) removal from natural water by co-precipitation with either ferric chloride or aluminum sulfate. The independent and interactive effects of factors including pH and co-precipitant concentration were investigated though the linear regression model obtained by Multiple Linear Regression (MLR) technique. For FFD, predicted removal efficiencies were calculated to plot the response surface. The optimized conditions at pH 7 and 225 mg/L of ferric ions were used to remove 90 mg/L of As(III), while alum sulfate was a poor co-precipitant for As(III) removal. In the case of As(V), 225 mg/L of ferric ions and 135 mg/L of aluminum ions were suitable co-precipitant doses to remove 90 mg/L of As(V) at pH 7. In addition, CCD was used to determine the main effects of pH, ferric ions and initial arsenic concentrations. Linear, quadratic and interaction parameters for the major factors were constructed in order to build the regression function, with coefficients calculated by MLR. The function was calibrated and validated using external experimental runs. The correlation coefficients (R^2) of the actual vs. predicted arsenic removal percentages were 0.9871 and 0.9478 for As(III) and As(V), respectively. Analysis of variance (ANOVA) was used to determine the significance level of these parameters. All major factors were determined to be significant, with *p*-values <0.01. Multi-layer response surfaces were developed to determine the best conditions, having highest removal efficiency. The maximum removal efficiencies for arsenic species were approximately 100%, achieved by model prediction with a ferric ion concentration of 225 mg/L at pH 7. These optimized conditions were then applied to remove arsenic from two industrial wastewater samples, giving efficiencies of 93.98, and 91.48%. The results reveal that the chosen conditions from the RSM approach are applicable for arsenic removal from real water samples.

Department:	Chemistry	Student's Signature	....
Field of Study:	Chemistry	Advisor's Signature	....
Academic Year:	2014	Co-Advisor's Signature	....

ACKNOWLEDGEMENTS

For achievement of this thesis, I would like to greatly express the appreciation to Assistant Professor Dr. Apichat Imyim as my advisor, Assistant Professor Dr. Kanet Wongravee as my co-advisor for their consultations, assistances, supports and encouragements. Furthermore, I would like to greatly express the appreciation to my thesis committees Associate Professor Dr. Vudhichai Parasuk, Assistant Professor Dr. Fuangfa Unob and Dr. Chatvalee Kalambaheti, for their valuable comments for improvement.

This thesis could not be successfully achieved without kindness and helpful of many people. I would like to be grateful to Assistant Professor Dr. Wanlapa Aeungmaitrepirom and all members of the Environmental Analysis Research Unit. Moreover, I would like to be grateful to PTT Public Company Limited, the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) and the Environmental Analysis Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University for financial support and facilities.

Finally, I am grateful to my family for everything and support throughout the entire education.

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LIST OF ABBREVIATIONS

As(III)	arsenite
As(V)	arsenate
mg L^{-1}	milligram per litre
μg L^{-1}	microgram per liter
CCD	central composite design
RSM	response surface methodology
mM	millimolar
mL	milliliter
^{o}C	celcius degree
min	minute
hrs	hours
rpm	revolutions per minute
%	percentage
TK80	coded name of wastes ample
TK81	coded name of wastes ample
ANOVA	analysis of variance

CHAPTER I

INTRODUCTION

1.1 State of problem

Arsenic is a metalloid and toxic element. It affects to the environment and human health as skin, lungs, kidney and liver cancer and other diseases [1]. Many millions people in a lot of countries has been suffering from arsenic toxicity contaminant in both natural ground and surface water [2]. Generally, arsenic is found in oxyanion inorganic forms: As(III) or arsenite (AsO_3^{3-}) and As(V) or arsenate (AsO_4^{2-}) [2]. In addition, industrial activities such as mining, agriculture, refinery process in petroleum industry and coal burning can discharge highly arsenic concentration into natural water [3]. Consequently, the World Health Organization (WHO) and the United States Environment Protection Agency (USEPA) have set a maximum contaminant level (MCL) for arsenic in drinking water as 10 $\mu g\ L^{-1}$. Moreover, the maximum contaminant level (MCL) for arsenic contaminant in industrial wastewater was set by the Ministry of Science and Technology of Thailand as 0.25 $mg\ L^{-1}$.

Several techniques for arsenic removal such as coagulation or co-precipitation [4-7], adsorption [8-11], filtration [12] and ion-exchange [13-15] have been studied. Co-precipitation is an effective technique for the removal of arsenic contaminants in water at high level of concentration and can be applied to eliminate arsenic contaminant in industrial wastewaters. Because of these reasons, researchers have been concentrating on optimizing the experimental conditions and evaluating the effect of parameters on arsenic removal by co-precipitation with ferric chloride and Alum or aluminum sulfate as coagulants [4-7]. In previous works, the efficiency of arsenic removal of above 90% have been reported for As(V) and As(III) [4-7]. However, ferric chloride and Alum as coagulants can eliminate As(V) better than As(III) at neutral pH range [7, 16]. Thus an oxidation process was employed to oxidize As(III) to As(V) before co-precipitation to increase the removal efficiency [17].

Generally, the optimized conditions for co-precipitation of arsenic are the major purpose [4, 6, 7]. The parameters such as types and amount of coagulant, pH range and coagulant aids were evaluated to find suitable conditions for the removal of arsenic by one factor at a time method [7]. However, the one factor at a time technique required high number of experiments to find the optimized conditions. Moreover, if the parameters or factors are correlated, this technique cannot find the best optimized conditions [18]. Hence, an experimental design with response surface methodology (RSM) is an effective technique to find the optimized conditions for removal of arsenic using a few numbers of experiments. Baskan and Para used the Box-Behnken design (BBD) approach with RSM to find the optimized conditions for only As(V) using ferric chloride [4] and aluminum sulfate [6].

In this research, full factorial design (FFD) and central composite design (CCD) were provided to evaluate the optimized conditions and the effect of each parameter on the efficiency of arsenic removal by co-precipitation using ferric chloride compared with aluminum sulfate.

1.2 Objective and scope of the research

The main objective of this work is to determine the optimized condition for evaluating the removal efficiency of As(III) and As(V) form wastewater by co-precipitation using ferric chloride and aluminum sulfate. The RSM methods including full factorial designs with three levels and the CCD method were applied to evaluate the highest removal efficiencies of both inorganic arsenic forms and investigate the main and interaction effects of factors or independent variables.

1.3 Benefit of the research

Obtaining the maximum efficiencies of the removal of inorganic arsenic species by the RSM techniques and the optimized conditions are applied to the elimination of arsenic in petrochemical wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Property of arsenic.

Recently, arsenic is also known as semi-metal element in periodic table. Arsenic is used in many industries such as refinery petroleum industry, pesticides, mining and wood treatments. However, arsenic is toxic element and its crisis occurs around the world.

Arsenic contaminant can be found both in organic and inorganic forms [2]. Naturally, oxyanion in inorganic forms as As(III) and As(V) as shown in Figure 2.1, is mostly found in ground and surface water. Whereas organic arsenic such as methylarsenite, dimethylarsenite, methylarsenate and dimethylarsenate, as shown in Figure 2.1, are mostly found in industrial wastewater [2].

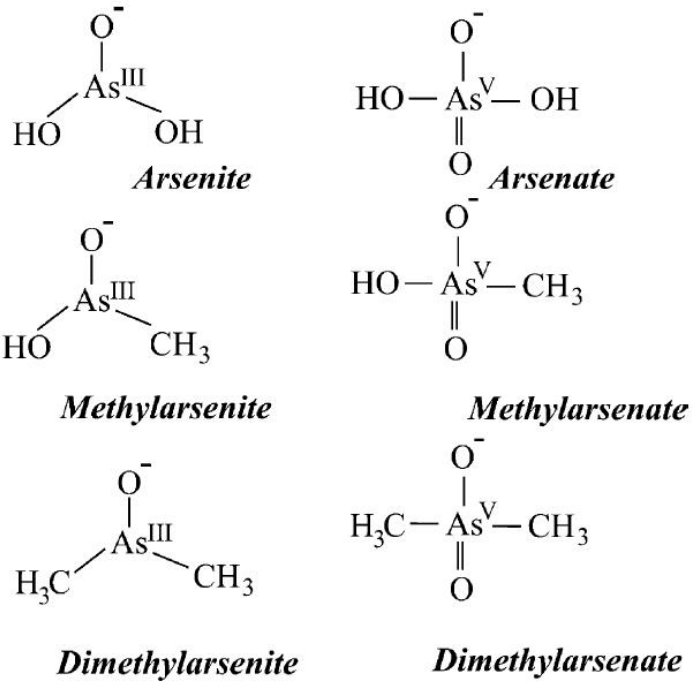


Figure 2.1 Molecular structure of arsenic in water [19]

Generally, the speciation of As(III) and As(V) depends on the range of pH [2] as shown in Figure 2.2 and correlated pK_a values of arsenic species are shown in Equations (2.1) – (2.6) [20].

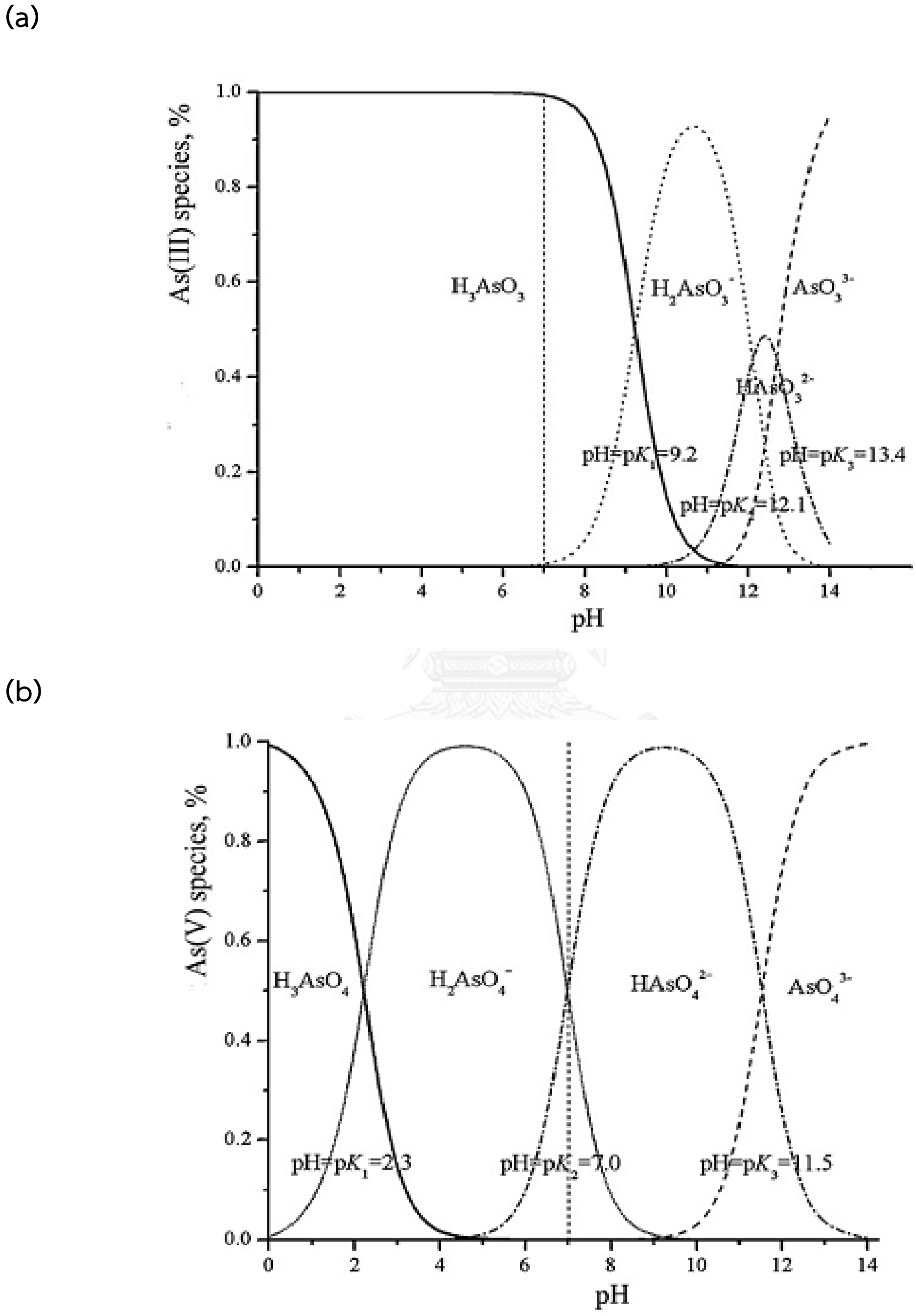


Figure 2.2 Speciation of arsenite (a) and arsenate (b) at range of various pH [21]

$$H_3AsO_3 \rightleftharpoons H_2AsO_3^- + H^+ \quad pK_a = 9.2 \qquad (2.1)$$

$$H_2AsO_3^- \rightleftharpoons HAsO_3^{2-} + H^+ \quad pK_a = 12.1 \qquad (2.2)$$

$$HAsO_3^{2-} \rightleftharpoons AsO_3^{3-} + H^+ \qquad pK_a = 12.7 \qquad (2.3)$$

Equations (2.1) – (2.3) express acidic dissociations of As(III) and pK_a values [20].

$$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+ \qquad pK_a = 2.3 \qquad (2.4)$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ \qquad pK_a = 6.8 \qquad (2.5)$$

$$HAsO_4^{2-} \rightleftharpoons AsO_4^{3-} + H^+ \qquad pK_a = 11.6 \qquad (2.6)$$

Equations (2.1) – (2.3) show acidic dissociations of As(V) and pK_a values [20].

2.2 Arsenic eliminated techniques in wastewater.

Arsenic has been widely used in pesticides in agriculture to control insect, industrial activities such as smelting of several ores and refinery operation process. These utilizations have released a high level of arsenic contaminant. Thus arsenic removal process is necessary to be used in these industries. Several techniques for arsenic removal are being investigated such as oxidation, ion exchange, filtration, adsorption and co-precipitation. These techniques will be shortly explained as follows.

2.2.1 Oxidation

Arsenate is a pentavalent oxyanion form that can be easier removed than other forms. In fact, industrial wastewater does not comprise only arsenate contaminant but consists of organic forms (dimethylarsenate, methylarsenite) and arsenite. Hence, the oxidation process is important to convert organic arsenic and arsenite to arsenate before removing arsenic.

Oxidation is part of a pretreatment step in water treatment which the chemical reaction involves an increase in oxidation number of metal element by adding oxygen atom from an oxidant to arsenic compound, Equation (2.7) [22]. Sodium hypochlorite, potassium permanganate, chlorine dioxide and monochloramine were mostly used as oxidants in chemical oxidation process [22].

$$H_3AsO_3 + NaClO \longrightarrow H_2AsO_4^- + Na^+ + Cl^- + H^+ \qquad (2.7)$$

Besides chemical oxidation, other types of oxidation have been widely used such as microbiological oxidation [23] and photochemical oxidation [24]. However, the oxidation pretreatment can only change arsenic form to another one but cannot remove arsenic from wastewater. Hence, the oxidation process has to be combined with other processes to remove arsenic in the water treatment.

2.2.2 Ion exchange

An ion exchange technique has been widely applied for the elimination of arsenic from water. When arsenic contaminated water is passed through a column, arsenic can be exchanged with the anion moieties present on the strong anion exchanger or resin [25]. Additionally, the ion exchange technique can separate arsenic species in water [26]. The advantages of ion exchange technique are using a less space of instrumental operation, high efficiency and less time of operation. However, the ion exchange technique is not suitable for removal of arsenic at high concentration because of its limitation of capacity of ion exchange resin. Therefore, the ion exchange is suitable for treatment of water of low degree of arsenic contamination such as drinking water treatment.

2.2.3 Filtration

Filtration is a technique using a filter or membrane to trap arsenic from contaminated water. Therefore the pore size and types of membrane is important for this technique. Generally, the filtration combined with the precipitation and flocculation processes have been used to remove arsenic from contaminated wastewater [5].

2.2.4 Adsorption

Adsorption has been mostly studied for the removal of arsenic because adsorption is an economical technique for the removal of arsenic with high efficiency and simple operation. The most important feature of this technique is an adsorbent because the removal efficiency depends on the chemical and physical property, surface area, pore size, surface polarity and functional group on the adsorbent.

Several adsorbents such as activated carbon [10], polymeric adsorbent [27], resin [28], activated alumina [29], sand [9], red mud [30] have been investigated to remove arsenic contaminant from wastewater. A mechanism of adsorption consists of 2 types as known as the physical adsorption, in which the adsorbate attaches to the adsorbent via Van Der Waal's force, and the chemical adsorption, in which adsorbed species are adsorbed by chemical bonding with functional groups on the adsorbent. Therefore, the interaction force of chemical adsorption is stronger than that of physical adsorption.

2.2.5 Co-precipitation

Arsenic removal by co-precipitation is an economically effective technique for the removal of arsenic at high levels of contamination. Additional turbidity and color of water can be also eliminated while removing arsenic by co-precipitation. Therefore, the co-precipitation has been mostly used as a pretreatment in tap water production and treatment of industrial wastewater. Co-precipitants play an important role in co-precipitation. It determines the removal efficiency. Ferric chloride and alum or aluminum sulfate are effective and economical coagulants for the removal of arsenic form contaminated wastewater.

Basically, the mechanism of co-precipitation of arsenic using ferric chloride and aluminum sulfate was explained as follows:

Firstly, the dissolution of co-precipitant in arsenic contaminated water. Oxyanion arsenic species can form precipitates and/or complexes with ions of co-precipitant as ferric ion (ferric chloride) and aluminum ion (aluminum sulfate) and become the forms of ferric arsenite ($FeAsO_3$), ferric arsenate ($FeAsO_4$), aluminum arsenite ($AlAsO_3$) and aluminum arsenate ($AlAsO_4$) as known as nuclei particles in a nucleation step. The formations of inorganic arsenic precipitates with co-precipitants are shown in Equations (2.8) – (2.11):

$$Fe^{3+}(aq) + AsO_3^{3-}(aq) \rightleftharpoons FeAsO_3(s) \qquad (2.8)$$

$$Fe^{3+}(aq) + AsO_4^{3-}(aq) \rightleftharpoons FeAsO_4(s) \qquad (2.9)$$

$$Al^{3+}(aq) + AsO_3^{3-}(aq) \rightleftharpoons AlAsO_3(s) \qquad (2.10)$$

$$Al^{3+}(aq) + AsO_4^{3-}(aq) \rightleftharpoons AlAsO_4(s) \qquad (2.11)$$

$$Fe^{3+}(aq) + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+ \qquad (2.12)$$

$$Al^{3+}(aq) + 3H_2O \rightleftharpoons Al(OH)_3(s) + 3H^+ \qquad (2.13)$$

In the next step of co-precipitation, the nuclei particles grow to be larger particles as known as colloidal particles by an aggregation of several nuclei particles and agglomerate together. At the same time, arsenic ions are adsorbed onto the surface via inner sphere complexation [31, 32]. In addition, ferric ions and aluminum ions can be commonly formed in solid forms of ferric hydroxide and aluminum hydroxide as expressed in Equations (2.12), (2.13). Oxyanion arsenic species can be adsorbed on these metal oxide via inner sphere complexation [32] as shown by Equations (2.14) – (2.17) and Figure 2.3 [31]. A simultaneous precipitation by ferric compounds or aluminum compounds is called “co-precipitation”.

$$Fe(OH)_2(OH)(s) + H_3AsO_3(aq) \rightleftharpoons (Fe(OH)_2HAsO^-_3)(s) + H^+(aq) + H_2O \qquad (2.14)$$

$$Fe(OH)_2(OH)(s) + H_3AsO_3(aq) \rightleftharpoons (Fe(OH)_2HAsO^{2-}_4)(s) + 2H^+(aq) + H_2O \qquad (2.15)$$

$$Al(OH)_2(OH)(s) + H_3AsO_3(aq) \rightleftharpoons (Al(OH)_2HAsO^-_3)(s) + H^+(aq) + H_2O \qquad (2.16)$$

$$Al(OH)_2(OH)(s) + H_3AsO_3(aq) \rightleftharpoons (Al(OH)_2HAsO^{2-}_4)(s) + 2H^+(aq) + H_2O \qquad (2.17)$$

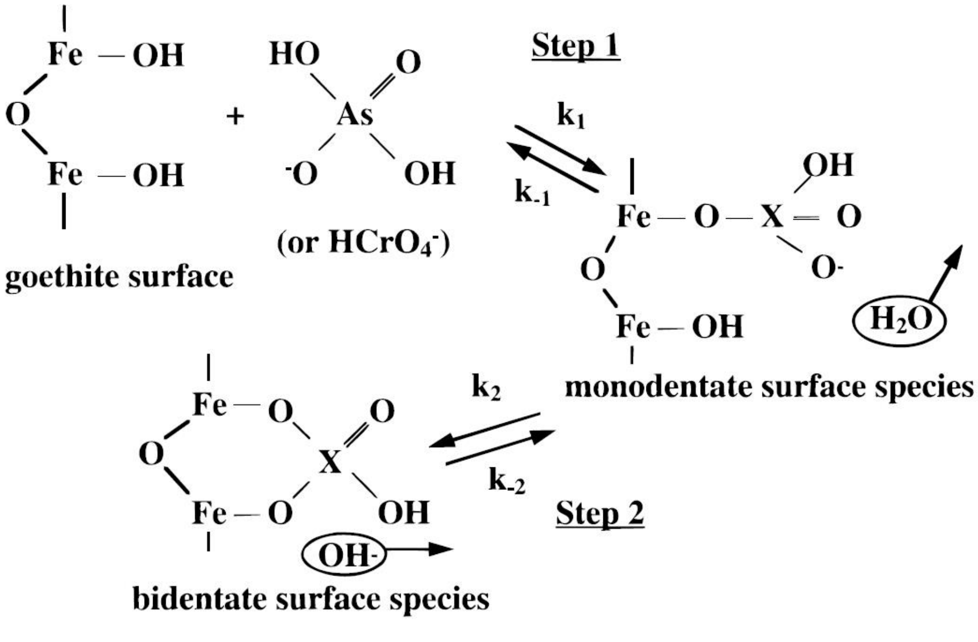


Figure 2.3 Mechanism of adsorption of arsenate on metal oxide [31].

At certain range of pH, the co–precipitation mechanism can be described by Equations (2.18) - (2.21)

$H_2AsO^-_3(aq) + Fe(OH)_3(s) \rightleftharpoons$ Fe – As complex(s) + $OH^-(aq)$ (2.18)

$H_2AsO^-_4(aq) + Fe(OH)_3(s) \rightleftharpoons$ Fe – As complex(s) + $OH^-(aq)$ (2.19)

$H_2AsO^-_3(aq) + Al(OH)_3(s) \rightleftharpoons$ Al – As complex(s) + $OH^-(aq)$ (2.20)

$H_2AsO^-_4(aq) + Al(OH)_3(s) \rightleftharpoons$ Al – As complex(s) + $OH^-(aq)$ (2.21)

According to the mechanism of co-precipitation of arsenic using ferric ions and aluminum ions as shown in Equations (2.18) – (2.21), the important factors for the successful arsenic removal are the pH of solution, the co-precipitant and initial arsenic concentration. It can be expected that the ratio of amount of co-precipitant and initial arsenic should be high to completely remove arsenic from contaminated water by co–precipitation. In addition, the pH value can affect on the efficiency of arsenic removal as the speciation of arsenite and arsenate in water is controlled by pH [33]. These factors are correlated and affect on the efficiency of arsenic removal. Hence, the determination of optimized conditions of only these major factors using one factor at a time method for efficient removal of arsenic cannot find the maximum efficiency. For these systems, interactive effect of major factors should be determined for the maximum efficiency of arsenic removal using any statistical technique.

2.3 experimental designs and response surface methodology

An optimization refers to making an improvement of chemical reaction or obtaining the maximum efficiency of a process. The optimization has been generally used in analytical chemistry to set up the best experimental conditions discovering which the maximum response is expected and finally it has been applied to real samples.

Traditionally, the optimization in analytical field has been commonly investigated by monitoring the effect of only one factor on efficiency of experimental response, while the others factors are fixed at a constant level. This approach called as “one factor at a time” can obtain the maximum response if the factor does not interact with other factors in experiments. In fact, most experiments are systematic with interactions of factors. Therefore, an “one factor at a time” cannot obtain the maximum response [18]. Moreover, the “one factor at a time” has a lot of disadvantages such as exploring the maximum response with high number of experiments and taking a long time. Response surface methodology (RSM) with experimental design are alternative approach [18] as a statistical method that evaluate the interactive effects of the main factors or independent variables correlated to the response. Moreover, there are a lot of advantages of using the RSM with experimental design in chemical experiments. The definition of term “RSM” employed in experimental design field is discussed in the next paragraph.

2.3.1 Advantages of experimental design [18].

2.3.1.1 Screening. Using experimental design can investigate important factors which strongly influence on the response by evaluating coefficient of each factor from linear regression equation (will be discussed in Section 2.3.3). Furthermore, unimportant factor can be ignored because it does not affect on the response.

2.3.1.2 Optimization. Using experimental design is commonly applied to discover the optimized conditions in chemical field such as improving the highest yield of synthetic chemical reaction, separation in chromatography field and removal of toxic agent in environmental field. The optimization can be explored by evaluating the RSM (will be discussed in Section 2.3.3).

2.3.1.3 Saving time. Generally, experimental design is an approach which investigates the optimized conditions with a minimized number of experiments. For this reason, the RSM with experimental design is an extensive technique.

2.3.1.4 Quantitative modeling. The RSM with experimental design is not only approach to explore the maximum response but also prediction of response without laboratory experiment.

2.3.2 Definition of words in the RSM with experimental design field

2.3.2.1 Response is a final experimental result which is interested in as a percentage of yields in organic synthesis or intensity of light in spectrophotometry. There are two types of response; firstly, an observed response is experimental result. Another, predicted response is the response that is achieved from calculating a regression model. For this research the efficiency of removal of arsenic is the response.

2.3.2.2 Factor or independent variable is a parameter which affects on the response. Factors can affect positively on the response by increasing response when increasing a level of factors. Conversely, factors can affect positively on the response by increasing response when decreasing a level of factors.

2.3.2.3 Actual value represents the level of each factor such as amount of arsenic is mg L^{-1} as unit or temperature is Celsius degree as unit.

2.3.2.4 Code value represents the level of factor. The level of factor (actual value) is replaced by coded value and uses code value to calculate the regression model.

There are several designs which are used in chemistry field such as full factorial design, fractional factorial design, Plackett-Burman and Taguchi design, Box-Behnken statistical design and central composite design. Each design has advantages and disadvantages; choosing a design depends on a chemical system and a number of factors influencing the system of interest. If the number of main factors is high, some experimental designs are not suitable due to high number of experimental runs. For this research, full factorial design at 3 levels and central composite design were used to access the optimized condition for arsenic removal.

2.3.3 Full factorial design

Generally, full factorial designs at two levels are applied to screen the factors [18]. Sometime full factorial designs are used to obtain maximum response with the best condition by using 3 levels. The number of experiments of full factorial designs is achieved by

$$N=l^k \qquad (2.22)$$

Where N is the number of experiments,

l is the number of levels,

k is the number of factors or independent variables.

For example, full factorial design for 2 factors consists of factor A and factor B at 3 levels (low, medium and high level) is used to evaluate individual factors, interactive factors and discover the maximum removal efficiency. Therefore, the number of experiments is 9 experiments. The following processes are used to carefully construct the design of the experiments and evaluate the results.

Firstly, the high medium and high level is chosen for each factor, for this example, a1, a2 and a3 is low, medium and high level of factor A. For factor B, b1, b2 and b3 is low, medium and high level, respectively.

The second step, the actual values are replaced by the coded value for each factor. At low, medium and high level is replaced by -1, 0 and +1 (coded value), respectively as shown in table 2.1 and figure 2.4;

Table 2.1 Levels of each factor

factor	Actual value of level			Coded value of level		
	low	medium	high	low	Medium	high
A	a1	a2	a3	-1	0	+1
B	b1	b2	b3	-1	0	+1

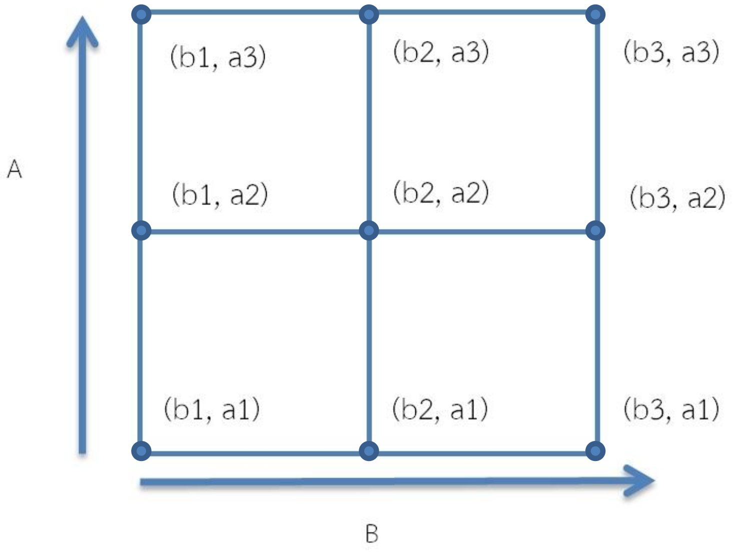


Figure 2.4 Two dimension of full factorial design at 3 levels

The third step, a predicted percentage of removal of arsenic (response) can be evaluated as a function as shown in Equation (2.23);

$$y=f(X_1,X_2,X_3,...,X_n) \qquad (2.23)$$

where y is the response arsenic removal of the system.

$X_1,X_2,X_3,...,X_n$ are the individual factors.

For this research, a quadratic regression model, consists of the main or individual, interactive and second order polynomial terms in a regression model, was used to obtain removal efficient prediction of the function as shown in Equation (2.24);

$$y = b_0+\sum b_iX_i+\sum b_{ii}X_i^2+\sum b_{ij}X_iX_j \qquad (2.24)$$

where $\boldsymbol{y}$ is the response arsenic removal of the system.

b_0 is the constant coefficient (intercept in linear equation)

b_i**,** b_{ii}**,** b_{ij} are the coefficient in the linear quadratic and interaction terms in equation, respectively.

After choosing the type of regression model, the observed responses are gotten from experiments at each condition of design as shown in Table 2.2. For evaluating interactive and quadratic terms, these values are evaluated by multiplying the coded value of each main factor as shown in the design matrix in Table 2.2. For data in Table 2.2, the values of observed response (y) and all of factor (all of X) are added in Equation (2.24). Therefore, there are 9 equations for this design (9 experiments) and 6 parameters (b_0, b_1, b_2, b_{11}, b_{22}, and b_{12}) for each equation. These parameters can be evaluated by design matrix as shown in Figure 2.5 and Equation (2.25)

Table 2.2 The design matrix for full factorial design

number of experiment	Intercept X_0	pH X_1	Fe X_2	pH^2 X_1^2	Fe^2 X_2^2	pH Fe X_1X_2	observed response (y)
1	1	-1	-1	1	1	1	$Y1$
2	1	0	-1	0	1	0	$Y2$
3	1	1	-1	1	1	-1	$Y3$
4	1	-1	0	1	0	0	$Y4$
5	1	0	0	0	0	0	$Y5$
6	1	1	0	1	0	0	$Y6$
7	1	-1	1	1	1	-1	$Y7$
8	1	0	1	0	1	0	$Y8$
9	1	1	1	1	1	1	$Y9$

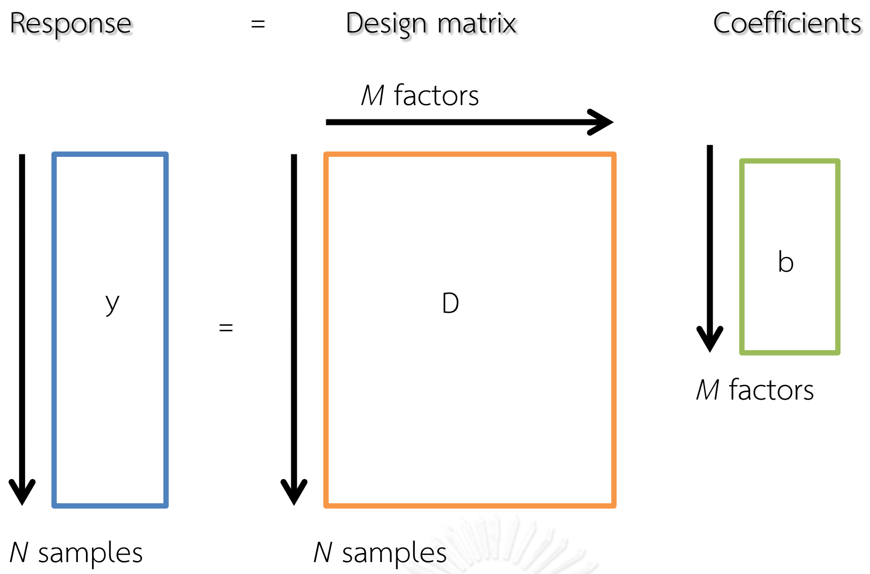


Figure 2.5 Solution of obtaining coefficient by using design matrix

$$\underset{(N\times 1)}{y} = \underset{(N\times M)}{D} \cdot \underset{(M\times 1)}{b}$$

$$\underset{(M\times N)}{D^T}\ \underset{(N\times 1)}{y} = \underset{(M\times N)}{D^T} \cdot \underset{(N\times M)}{D} \cdot \underset{(M\times 1)}{b}$$

$$\underset{(M\times M)}{(D^T.D)^{-1}}\ \underset{(M\times N)}{D^T}\ \underset{(N\times 1)}{y} = \underset{(M\times M)}{(D^T.D)^{-1}}\ \underset{(M\times M)}{(D^T.D)}\ \underset{(M\times 1)}{b}$$

$$\underset{(M\times M)}{(D^T.D)^{-1}}\ \underset{(M\times N)}{D^T}\ \underset{(N\times 1)}{y} = \underset{(M\times 1)}{b} \tag{2.25}$$

Where y is observed response,

D is design matrix,

b is coefficient of equation,

N is number of experiments,

M is number of coefficients.

For Figure 2.5, the coefficients were solved. Therefore, the quadratic regression model shown in Equation (2.26) can be presented the predicted response (removal efficiency of arsenic).

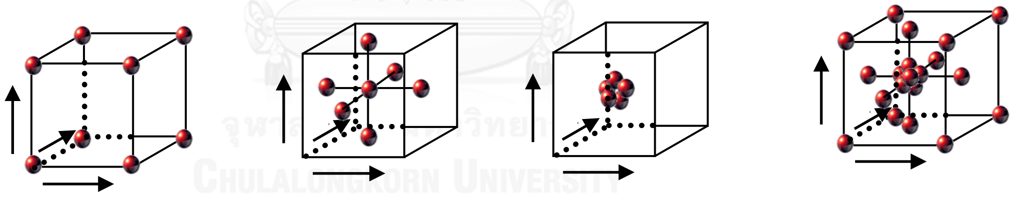
$$y=b_0+b_1X_1+b_2X_2+b_{11}X_1^2+b_{22}X_2^2+b_{12}X_1X_2 \tag{2.26}$$

When achieving the regression model as Equation (2.26), the predicted responses are calculated to construct the response surface (RSM) to discover the maximum response at the optimized condition.

Although full factorial design at 3 levels is a simple design, high number of factor in the system is limitation for full factorial design at 3 levels because the number of experiments is very large as expressed in Equation (2.22). For instance, the design is evaluated with 5 factors at 3 levels. Thus, this design involves 3^5 or 243 experiments. In addition, full factorial design cannot get replicate information and cannot provide the predicted response outside the design region. Hence, a central composite design (CCD) at 3 or 4 factors is an alternative design to explore the maximum response.

2.3.4 Central composite design (CCD)

The central composite design (CCD) has been commonly used in chemistry field. Figure 2.6 shows a set up of the design with 3 factors.



Full factorial star Replication The CCD

Figure 2.6 Each point for the central composite design with 3 factors [18]

For the Figure 2.6, there are 20 points or experiments for the CCD with 3 factors consisting of 8 points for factorial points, 7 points for star point and 5 points for replication point.

- The factorial point in the CCD provides an evaluation of all interactive terms [18]. These points are in the corners of a cube. All of these points combine with +1 and -1 as the coded value. The number of experiments for factorial point is 2^k where k is a number of factors. Therefore, the CCD with 3 factors involves 8 experiments for factorial points or 12 experiments for 4 factors which cannot visualize the cube.

- The star point can be used to evaluate the squared terms. For evaluating the squared terms, more than 2 levels for each factor are required. These points combine with $+a$, 0 and $-a$. For each point, a factor is at level $\pm a$ and the other factors are at level 0. The a value of coded value depends on the number of factors in the system as shown in Table 2.3. The number of experiments for star point is $2K +1$ where k is a number of factors. Therefore, the CCD with 3 factors involves 7 experiments for factorial points or 9 experiments for 4 factors which cannot visualize the cube as same as the factorial point.

Table 2.3 Information of a value and factorial portion for each number of factors [18]

Number of factors	Scaled value for a
2	1.414
3	1.682
4	2.000

- Finally, the replication point is used to investigate the experimental error typically 5 (*R)* points at center point as medium level (0) for each factor.

The total number of experiments of the CCD can be shown by Equation (2.27) and the construction of the CCD for 3 factor is shown in table 2.4;

$$N = 2k + (2K + 1) + R \tag{2.27}$$

Where N is a number of experiments of the CCD,

k is a number of factors,

R is a number of replicated experiments.

Table 2.4 Construction of the CCD for 3 factors

Factorial		
1	1	1
1	1	-1
1	-1	1
1	-1	-1
-1	1	1
-1	1	-1
-1	-1	1
-1	-1	-1
.		
Star		
0	0	-1
0	0	1
0	1	0
0	-1	0
1	0	0
-1	0	0
0	0	0

Replication		
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

For evaluating the quadratic regression model, it can be calculated by using Equations (2.23, 2.25) similarly to the solution in full factorial design. The quadratic regression model of the CCD at 3 factors is shown in Equation 2.28;

$$y=b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \tag{2.28}$$

2.3.5 Analysis of variance

Furthermore, the analysis of variance (ANOVA) is used to evaluate the sufficiency of the model and the significance of each coefficient number in the quadratic regression model of the full factorial design and the CCD. The models and coefficient number are significant when their F-values and probability values are high. There are several values in ANOVA table. These values can be calculated by these equations;

- Degree of freedom for experiment

$$df=N - P - R \tag{2.29}$$

when *df* is a degree of freedom,

N is a number of experiments,

P is a number of coefficients,

R is a number of replications.

- Degree of freedom for ANOVA.

Where *df* of model **=** *P* **–** ***1***

df of parameters = 1

df of total = *N* **–** ***1***

df of residual **=** (*df* of total) **–** (*df* of model)

df of lack of fit **=** (*df* of total) **–**(*df* of resicdual)

df of pure error = (*df* of resicdual) – (*df* of lack of fit)

- Sum of squares

$$SST = \sum\left(y - \bar{y}\right)^2 \qquad (2.31)$$

$$SSR = \sum\left(y' - \bar{y}'\right)^2 \qquad (2.32)$$

$$SSE = \sum\left(y - \bar{y}'\right)^2 \qquad (2.31)$$

Where *SST* is a sum of squares total,

SSR is a sum of squares regression,

SSE is a sum of squares error,

y is a observed response,

$\bar{y}$ is a mean of observed response,

y' is a predicted response,

$\bar{y}'$ is a mean of predicted response.

- Mean squares

$$\text{Mean squares} = \frac{\text{sum of squares}}{\text{df}}$$

- *F* value

$$F \text{ value} = \frac{\text{mean squares}}{\text{mean squares of residual}}$$

- *p* value is a probability of deny to null hypothesis which calculate from *F* value.

2.4 Literature review

Co-precipitation or coagulation is a potential water treatment process which generally uses to treat industrial wastewater because it can eliminate color and colloidal particles including toxic metal with low cost and simple operation. For co-precipitation process, a co-precipitant plays necessary role. It is a determinant of removal efficiency. Ferric chloride and alum or aluminum sulfate are effective and economical co-precipitant for the removal of contaminants in water.

For using ferric chloride and aluminum sulfate as co-precipitation for removal arsenic contaminated water, in previous researches, the efficiency of arsenic removal of higher than 90% have been reported for As(V) and As(III) [4-7]. However, ferric chloride and aluminum sulfate employed as coagulants can remove As(V) more efficiently than As(III) at neutral pH range [7, 16].

Hering et al. [16] studied the removal of 20 µg L^{-1} of As(V) and As(III) from surface water using ferric chloride and aluminum sulfate. The efficiencies of As(V) removal was above 90% and ferric chloride showed a potential to remove arsenic in wider pH range than aluminum sulfate. Conversely, the efficiency of As(III) removal was lower than As(V) for both ferric chloride and aluminum sulfate.

Qiao et al. [7] studied the effects of pH, ratio of As/Fe and initial concentration of arsenic on As(V) and As(III) removal using ferric chloride as coagulant. The efficiency of arsenic was high when decreasing the ratio of As/Fe. However, the efficiency of As(V) removal was higher than As(III) at optimized pH range. Moreover, phosphate, sulfate and silicate anions had the effect of competing ions on co-precipitation of arsenic. Phosphate had the most significant effect on co-precipitation of arsenic due to the fact that its structure is tetrahedral which is the same as arsenic and it has highly negative charge (-3) while sulfate’s charge is (-2). For the effect of silicate, it had minor effect on co-precipitation of arsenic. Comparing the effect of competing ions on co-precipitation of As(V) with As(III), the effect of competing ions on co-precipitation of As(III) has more significant than that of As(V).

Hence, pre-oxidation is an important process for removing As(III) by co-precipitation [17]. As(III) can be oxidized by $KMnO_4$ to As(V). After that, As(V) can be precipitated by ferric ions acting as co-precipitant [17]. Furthermore, other metal ions can precipitate arsenic such as calcium [34] and manganese [35].

Using The RSM with experimental design approach can be employed to obtain a maximum efficiency of arsenic removal. The experimental designs have been widely used in this regards;

Simsek et al. [36] used Box-Behnken experimental design (BBD) to assign the maximum adsorption capacity of As(V) onto iron-aluminum binary oxide-doped clinoptilolite. The maximum adsorption capacity of As(V) of 6.81 mg g^{-1} was found by the RSM at the optimized condition (pH = 6, temperature = 62 degree Celsius and initial As concentration = 9.4 mg L^{-1}).

Tuna et al. [37] have achieved the optimized condition to remove arsenic using activated carbon-based iron-containing adsorbents by the RSM with the BBD. For iron(II)-loaded activated carbon as hybrid adsorbents, the optimized conditions were pH 3.1, 63.68 degree Celsius and 8.4 mg L^{-1} of concentration of initial arsenic, while the optimized conditions of iron(III)-loaded activated carbon were pH 3.07, 25.25 degree Celsius, and 8.28 mg L^{-1} of concentration of initial arsenic.

For using the CCD to find out the optimized conditions to remove toxic metal, Bajpai et al. [38] have gained the optimized conditions for the removal of Cr(VI) by adsorption using weakly anion resin. The maximum efficiency was 93.26% at temperature of 30 degree Celcius and 250 rpm of speed of stirrer, contact time of 62.5 min, pH of 1.96, 145.4 mg L^{-1} of initial Cr (VI) concentration, and amount of resin of 8.51 g L^{-1}.

Based on the previous researches [36-38], the BBD and CCD were used to find out the maximum of efficiency for toxic metal removal by adsorption. For coagulation of arsenic, Bilici Baskan and Pala [4, 6] used the BBD to discover the maximum efficiency for As(V) removal using ferric chloride [4] and aluminum sulfate [6] at low level of arsenic concentration (10-1000 µg L^{-1}).

Hence, the objective of this work is to evaluate the removal efficiencies of As(III) and As(V) from water by ferric ions using central composite design (CCD) and study the main effects including ferric ion concentration, pH, and arsenic concentration, on the removal process. The key advantages of our study are the discovery of an optimized condition for simultaneous removal of As(III) and As(V) with the high removal efficiencies without any pre-oxidation requirement. The regression function of the removal efficiency relating to the factors mentioned above was obtained using Multiple Linear Regression (MLR), with calibration and validation steps demonstrated using external experimental runs to prevent problems of overfitting. Additionally, an alternative way to visualize the several response surfaces was developed using a superimposition approach for better viewing and interpretation. Using this, the optimized condition was determined as the condition having the highest removal efficiency as presented in the overlapped response surfaces for As(III) and As(V). The chosen condition was then applied to the removal of arsenic from set-up mixtures, and real waste water samples provided by a petrochemical company.

CHAPTER III

EXERIMENTAL

3.1 Analytical instruments

Instruments used in this research were listed in table 3.1.

Table 3.1 List of instruments

Instruments	Model, manufacturer
Inductively couple plasma optical emission spectrometer (ICP-OES)	iCAP 6500, Thermo Scientific
pH meter	Ultrabasic, DENVER
Transfer pipette	Brand
Stirrer	MS101,GEM
Centrifuge	CENTAUR 2, Sanyo
Sonicator	CREST
Jar test	FC6S, VELP@Scientifica

The Conditions for ICP-OES measurement is listed in Table 3.2

Table 3.2 Conditional parameters for ICP-OES

Parameters	Conditions
Wave length (nm)	189.042
Radio frequency power (W)	1150
Auxiliary gas flow (L min^{-1})	0.5
Nebulizer gas flow (L min^{-1})	0.6
Coolant gas flow (L min^{-1})	12
Plasma view	Axial
Repeatability (times)	3

3.2 Chemicals

All chemicals used in this research were summarized in table 3.3. They are analytical grade and were used without further purification.

Table 3.3 Chemicals list

Chemical	Supplier
The stock solution of 1000 mg As(V)/L	Merck
Sodium (meta)arsenite	Sigma-Aldrich
Hydrochloric acid 65%	Merck
Sodium hydroxide	Merck
Anhydrous Ferric chloride	Merck
Aluminum sulfate	Merck

3.3 Co-precipitation process

Ferric chloride or aluminum sulfate was added, in separate experiments, to 10 mL of arsenic solution (each containing different concentrations of arsenic) followed by pH adjustment (HCl and/or NaOH). After that, the mixed solution was stirred rapidly for few minutes, followed by slow agitation for 30 min, and then followed by a precipitation time of 30 min. After co-precipitation, the solution was centrifuged at 3200 rpm for 10 min, and the supernatant was stored for arsenic determination using ICP-OES.

3.4 Evaluating parameters using one factor at a time

The parameters which affected on the removal efficiencies of As(III) and As(V) such as pH, type of co-precipitants and time consuming in settling process, were studied by using the “one factor at a time” method.

3.4.1 Effect of solution pH and type of co-precipitant

The effect of pH on the removal efficiencies of As(III) and As(V) was evaluated by varying the pH of the arsenic solution and the concentration of co-precipitant (ferric ion as 150 mg L^{-1} and aluminum ion as 90 mg L^{-1}). The concentration of arsenic was fixed at 90 mg L^{-1}. HNO_3 and NaOH were used to adjust the pH of solution.

3.4.2 Effect of setling time

The settling time was studied by varying the settling time between 30 min – 5 hrs. The concentrations of As(V) and ferric chloride were both fixed at 90 mg L^{-1}.

3.5 Full factorial design experimental

In this research, the co-precipitation of arsenic as 90 mg L^{-1} with ferric chloride and aluminum sulfate using the full factorial designs at 3 levels were studied. There are 4 designs including;

3.5.1 Full factorial deisgn of uisng ferric chloride for removing As(III).

The factors and each parameter level are shown in Table 3.4 and 3.5.

Table 3.4 Coded and actual values of each level in the full factorial design for As(III) removal with $FeCl_3$

factor	level		
	-1	0	1
pH	4	6.5	9
Fe ion conc. (mg L^{-1})	75	150	225

Table 3.5 Coded and actual values of each parameter and number of experiments (run) in the full factorial design for As(III) removal with $FeCl_3$

run	pH (X_1)		Fe conc. (mg L^{-1}) (X_2)	
	actual	code	actual	code
1	5	-1	75	-1
2	7.5	0	75	-1
3	10	1	75	-1
4	5	-1	150	0
5	7.5	0	150	0
6	10	1	150	0
7	5	-1	225	1
8	7.5	0	225	1
9	10	1	225	1

3.5.2 Full factorial design of using ferric chloride for removing As(V)

The factors and each parameter level are shown in Table 3.6 and 3.7.

Table 3.6 Code and actual value of each level in the full factorial design for As(V) removal with $FeCl_3$

factor	level		
	-1	0	1
pH	4	6.5	9
Fe ion conc. (mg L^{-1})	75	150	225

Table 3.7 Coded and actual values of each parameter and number of experiments (run) in the full factorial design for As(V) removal with $FeCl_3$

run	pH (X_1)		Fe conc. (mg L^{-1}) (X_2)	
	actual	code	actual	code
1	4	-1	75	-1
2	6.5	0	75	-1
3	9	1	75	-1
4	4	-1	150	0
5	6.5	0	150	0
6	9	1	150	0
7	4	-1	225	1
8	6.5	0	225	1
9	9	1	225	1

3.5.3 Full factorial design of using aluminum sulfate for removing As(III)

The factors and each parameter level are shown in Table 3.8 and 3.9.

Table 3.8 Code and actual value of each level in the full factorial design for As(III) removal with aluminum sulfate

factor	level		
	-1	0	1
pH	5	7.5	10
Al ion conc. (mg L^{-1})	45	90	135

Table 3.9 Coded and actual values of each parameter and number of experiments (run) in the full factorial design for As(III) removal with aluminum sulfate

run	pH (X_1)		Al conc. (mg L^{-1}) (X_2)	
	actual	code	actual	code
1	5	-1	45	-1
2	7.5	0	45	-1
3	10	1	45	-1
4	5	-1	90	0
5	7.5	0	90	0
6	10	1	90	0
7	5	-1	135	1
8	7.5	0	135	1
9	10	1	135	1

3.5.4 Full factorial design of using aluminum sulfate for removing As(V)

The factors and each parameter level are shown in Table 3.10 and 3.11.

Table 3.10 Coded and actual value of each level in the full factorial design for As(V) removal with aluminum sulfate

factor	level		
	-1	0	1
pH	4	6.5	9
Al ion conc. (mg L^{-1})	45	90	135

Table 3.11 Coded and actual values of each parameter and number of experiments (run) in the full factorial design for As(V) removal with alum

run	pH (X_1)		Al conc. (mg L^{-1}) (X_2)	
	actual	code	actual	code
1	4	-1	45	-1
2	6.5	0	45	-1
3	9	1	45	-1
4	4	-1	90	0
5	6.5	0	90	0
6	9	1	90	0
7	4	-1	135	1
8	6.5	0	135	1
9	9	1	135	1

For these 4 series of full factorial design, there are 3 replications in each point. Thus there are 27 experiments of each full factorial design at 3 levels.

3.6 Central composite experimental design

In this research, the central composite designs (CCD) were studied. There are 3 designs including;

3.6.1 CCD using ferric chloride for removing As(III)

Table 3.12 Coded and actual values of each level in the CCD for As(III) removal with $FeCl_3$

factor	level				
	-1.682	-1	0	1	1.682
pH	5	6	7.5	9	10
Ferric ion conc. (mg L^{-1})	23.85	75	150	225	276
initial Arsenic conc.(mg L^{-1})	14.55	45.45	90.91	136.36	167.27

Table 3.13 Coded and actual values of each parameter and number of experiments (run) in the CCD for As(III) removal with $FeCl_3$

run	pH (X_1)		Fe conc. (mg L^{-1}) (X_2)		Initial As conc.(mg L^{-1}) (X_3)	
	code	code	actual	code	actual	code
1	6	-1	75	-1	45	-1
2	9	1	75	-1	45	-1
3	6	-1	225	1	45	-1
4	9	1	225	1	45	-1
5	6	-1	75	-1	135	1
6	9	1	75	-1	135	1
7	6	-1	225	-1	135	1
8	9	1	225	1	135	1
9	7.5	0	150	0	90	0
10	7.5	0	23.85	-1.682	90	0
11	7.5	0	276	1.682	90	0
12	7.5	0	150	0	167.27	1.682
13	7.5	0	150	0	14.55	-1.682
14	5	-1.682	150	0	90	0
15	10	1.682	150	0	90	0

3.6.2 CCD using ferric chloride for removing As(V)

Table 3.14 Coded and actual values of each level in the CCD for As(V) removal with $FeCl_3$

factor	level				
	-1.682	-1	0	1	1.682
pH	4	5	6.5	8	9
Ferric ion conc. (mg L^{-1})	23.85	75.00	150.00	225.00	276.00
Initial Arsenic conc.(mg L^{-1})	14.55	45.45	90.91	136.36	167.27

Table 3.15 Coded and actual values of each parameter and number of experiments (run) in the CCD for As(V) removal with $FeCl_3$

run	pH (X_1)		Fe conc. (mg L^{-1}) (X_2)		Initial As conc.(mg L^{-1}) (X_3)	
	actual	code	actual	code	actual	code
1	5	-1	75	-1	45	-1
2	8	1	75	-1	45	-1
3	5	-1	225	1	45	-1
4	8	1	225	1	45	-1
5	5	-1	75	-1	135	1
6	8	1	75	-1	135	1
7	5	-1	225	1	135	1
8	8	1	225	1	135	1
9	6.5	0	150	0	90	0
10	6.5	0	23.85	-1.682	90	0
11	6.5	0	276	1.682	90	0
12	6.5	0	150	0	167.27	1.682
13	6.5	0	150	0	14.55	-1.682
14	4	-1.682	150	0	90	0
15	9	1.682	150	0	90	0

3.6.2 CCD using aluminum sulfate for removing As(V)

Table 3.16 Coded and actual value of each level in the CCD for As(V) removal with aluminum sulfate

factor	level				
	-1.682	-1	0	1	1.682
pH	4	5	6.5	8	9
Al ion conc. (mg L^{-1})	14.55	45.45	90.91	136.36	167.27
Initial Arsenic conc.(mg L^{-1})	14.55	45.45	90.91	136.36	167.27

Table 3.17 Coded and actual values of each parameter and number of experiments (run) in the CCD for As(III) removal with aluminum sulfate

run	pH (X_1)		Al conc. (mg L^{-1}) (X_2)		Initial As conc.(mg L^{-1}) (X_3)	
	actual	code	actual	code	actual	code
1	5	-1	45	-1	45	-1
2	7.9	1	45	-1	45	-1
3	5	-1	135	1	45	-1
4	7.9	1	135	1	45	-1
5	5	-1	45	-1	135	1
6	7.9	1	45	-1	135	1
7	5	-1	135	1	135	1
8	7.9	1	135	1	135	1
9	6.5	0	90	0	90	0
10	6.5	0	14	-1.682	90	0
11	6.5	0	167	1.682	90	0
12	6.5	0	90	0	167.27	1.682
13	6.5	0	90	0	14.55	-1.682
14	4	-1.682	90	0	90	0
15	9	1.682	90	0	90	0

For these 3 designs of the CCD, there are 3 replicates in each full factorial and star point. Moreover, there are 6 replicates in the center point. Thus there are 48 experiments of each CCD.

3.7 Removal arsenic in mixtures and real samples

The optimized conditions obtained from the RSM were used in removal mixtures of As(III) and As(V) in solutions and petrochemical wastewater samples as shown in table 3.18;

Table 3.18 Composition of arsenic mixture solutions and petrochemical wastewater

	Mixtures of As(III) and As(V)						Wastewaters		Natural water	
	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6	TK80	TK81	Spiked As(III)	Spiked As(V)
As(III) (mg L^{-1})	0.00	18.00	36.00	54.00	72.00	90.00	-	-	90.00	-
As(V) (mg L^{-1})	90.00	72.00	54.00	36.00	18.00	0.00	-	-	-	90.00
Total As (mg L^{-1})	90.00	90.00	90.00	90.00	90.00	90.00	66.31	68.16	90.00	90.00

3..8 Jar test

The co-precipitants were added in 500 mL of petrochemical wastewater TK81 in a beaker followed by stirrer operating at speed of 120 rpm for a min. After rapid mixing, the speed of stirrer operating was reduced to 20 rpm for 30 min and stop stirrer operating for allowing the settling of particles. The optimized conditions from the RSM were used in the Jar test.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preliminary study using one factor at a time method

4.1.1 Effect of pH on the efficiency of arsenic removal

First of all, the effect of pH on the efficiency of arsenic removal was investigated by employing one factor at a time method using ferric chloride and aluminum sulfate. The results are shown in Figure 4.1.

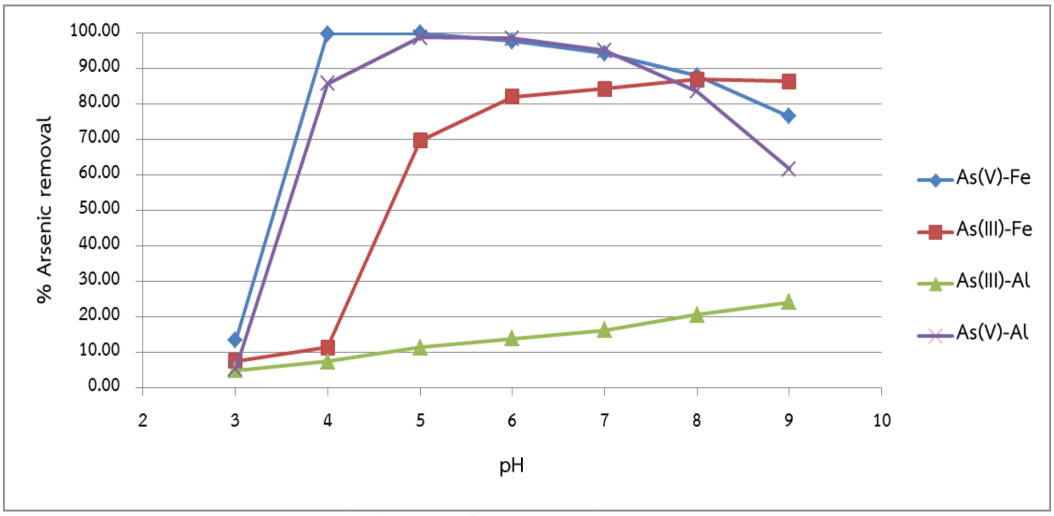


Figure 4.1 Effect of pH on As(III) and As(V) co-precipitation using ferric chloride and aluminum sulfate ([As] = 90 mg L^{-1}, [Fe^{3+}] = 150 mg L^{-1} (2.69 mM) and [Al^{3+}] = 90 mg L^{-1} (3.34 mM), total volume = 11 mL).

Considering the co-precipitation of As(V) using ferric chloride, the efficiency of As(V) removal was very poor at pH 3 and the efficiency dramatically increased to almost 99 % at the pH range of 4-5. When the pH increased from 5 to 9, its efficiency decreased. All of these results correlated to the speciation of As(V) in solution and the amount of positively charged co-precipitant (Fe^{3+}). According to Figure 2.2.b, neutral As(V) is predominant species in solution as H_3AsO_4 which is not precipitated by positively charged ferric ions at pH 3. Furthermore, there is no ferric hydroxide particle to adsorb As(V) at pH 3. Increasing pH 4 to 9, As(V) exits as $H_2AsO_4^-$ and $HAsO_4^{2-}$ (pKa_1 =2.3, pKa_2 = 6.9 as expressed in Equations (2.4)-(2.5), thus As(V) is more negatively charged when the pH increases. These negatively charged As(V) species can be precipitated with positively charged ferric ions via inner-sphere complexation [32] in the pH range of 4-9. However, the efficiency of As(V) removal decreased when increasing pH up to 9 because the predominant ferric hydroxide in the solution is negatively charged at high pHs. The electrostatic repulsion between ferric hydroxide and the negatively charged As(V) occurs.

For the precipitation of As(III) with ferric chloride, the efficiency of As(III) removal was very poor at the pH range of 3-4 and the efficiency dramatically increased to almost 70 % at pH 5 and increased slightly when increasing the pH from 5 to 9. For this result, it was different from that of As(V) because of the species distribution of As(III) in aqueous solution. According to Figure 2.2.a, the predominant neutral As(III) species (H_3AsO_3) is present in solution at the pH less than 9.2 (pKa_1 = 9.2) and the negatively charged As(III) species ($H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}) are major species at the pH more than 9.2. For these reasons, the efficiency increased with increasing the pH of solution. However, the efficiency of As(III) removal is not the same as the efficiency of As(V) in the pH range of 5-8 because when increasing the pH, the abundance of cations to form precipitates with arsenic species decreased.

In the case of the precipitation of As(V) using aluminum sulfate, the result was the same as that of As(V) using ferric chloride. The same explanation can be valid in this case. Comparing the efficiencies of co-precipitants in the co-precipitation of As(V) in the pH range of 5-8 (Figure 4.1), the efficiencies of As(V) precipitation using ferric chloride and aluminum sulfate were not different. On the other hand, their efficiencies were similar, except that the amount of aluminum ions (3.34 mM) is more required than that of ferric ions (2.69 mM). Therefore, ferric chloride is more appropriate for the removal of As(V) than aluminum sulfate.

For As(III) removal with aluminum sulfate, the efficiency was low because of the speciation of As(III). Moreover, aluminum sulfate is not effective co-precipitant. They do not have sorption sites for As(III) adsorption.

4.1.2 Effect of settling time on the efficiency of arsenic removal

Several researchers have been interested in settling time, which is an important factor, to assess an equilibrium time in the co-precipitation system.

According to Figure 4.2, the effect of settling time was considered using ferric ions at 90 mg L^{-1} to precipitate 90 mg L^{-1} of As(V) solution at pH 5 (chosen from Figure 4.1). The settling time was varied from 30 min to 6 hours and the results of each settling time are shown in Figure 4.2. From this figure, the settling equilibrium time of As(V) were obtained after 30 min. Moreover, this settling equilibrium time was further used in the removal As(V) and As(III) with aluminum sulfate and ferric chloride.

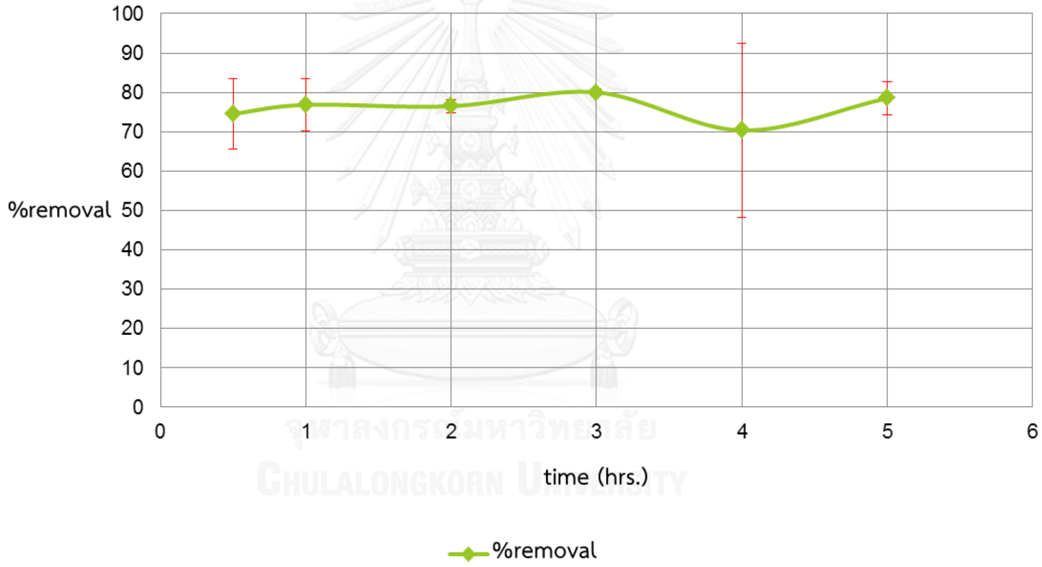


Figure 4.2 Effect of settling time on the efficiency of As(V) at 90 mg L^{-1} with 90 mg L^{-1} of ferric ions.

4.2 Full Factorial Design

In this research, full factorial designs at 3 levels were used to assess the maximum efficiencies of As(III) and As(V) and evaluate independent variables and interactive variables. From the Section 3.5, there are 4 sets of full factorial designs. Each design has 9 experiments of the number of experiments. In this research, there are 3 replications of each experiment. Therefore, the total number of experiments is 27 as shown in Table 3.4-3.10.

For a construction of the design, the factors of each level were constructed which were shown in Table 3.4, 3.6, 3.8 and 3.10 for the co-precipitation of As(III) and As(V) using ferric chloride and aluminum sulfate, respectively. The evaluating ranges of pH for the precipitation of As(III) is not the same as As(V) because of the speciation of arsenic. The predominant negatively charged species of As(III) is major species when the pH of solution is higher than 9.2. Therefore, the evaluating ranges of pH was set as pH 5-10. The predominant negatively charged As(V) is major species when the pH of solution is higher than 2.3. Thus the evaluating range of pH was set at the pH range of 4-9.

4.2.1 Regression models

When obtained the observed values from experiments of co-precipitation, the observed values (percentages of As removal) were shown in Table 4.1-4.2 and used to evaluate the regression model as shown in Equation (2.26) by using the multiple linear regression technique (MLR) which is discussed in Section 2.3.3. The quadratic regression models for each design are expressed in Equations (4.1)-(4.4) for the precipitation of As(III) and As(V) using ferric chloride and aluminum sulfate, respectively. The predicted values of the efficiencies (percentages of arsenic removal) were calculated using Equations (4.1)-(4.4) as shown in Tables 4.1-4.2.

The correlation coefficients (R^2) from the regression models exhibit a quality of fit of 0.9980, 0.9717, 0.9603 and 0.9900 for the precipitation of As(III) and As(V) using ferric chloride, As(III) and As(V) using aluminum sulfate, respectively. A correlation plot of the predicted against actual arsenic removal percentages is shown in Figure 4.3. The actual values are the measured response data for particular runs, and the predicted values were evaluated using the regression functions generated in Equations (4.1)–(4.4) to calibrate the model. In this study, we refer to this step as the model calibration. The results indicate that the model provides a sufficient representation of the real relationship among these variables. The accumulation of the points around the fitted line indicates a satisfactory correlation between the experimental data and the predicted values, demonstrating that the regression model is appropriate for predicting the response.

$$\%\text{As(III) removal} = 80.54+2.73X_1+18.79X_2-7.25X_1^2-6.91X_2^2+0.39X_1X_2 \quad (4.1)$$

$$\%\text{As(V) removal} = 97.75-13.10X_1+17.23X_2-9.84X_1^2-14.28X_2^2+5.51X_1X_2 \quad (4.2)$$

$$\%\text{As(III) removal} = 13.38+3.01X_1+1.77X_2-5.89X_1^2-0.42X_2^2+1.42X_1X_2 \quad (4.3)$$

$$\%\text{As(V) removal} =95.30-10.26X_1+16.13X_2-20.36X_1^2-9.43X_2^2+5.35X_1X_2 \quad (4.4)$$

Table 4.1 Observed and predicted values of full factorial design for % As(III) and As(V) removal with ferric chloride ([As] = 90 mg L^{-1})

run	coded		Ferric chloride			
	X_1	X_2	%As(III) removal		%As(V) removal	
			Observed	Predicted	Observed	Predicted
1	-1	-1	45.68±0.07	45.24	74.82±0.79	75.03
2	0	-1	54.47±0.58	54.84	68.14±0.59	66.24
3	1	-1	49.85±1.16	49.92	36.10±11.40	37.79
4	-1	0	69.59±0.29	70.56	99.78±0.05	101.02
5	0	0	81.43±0.57	80.54	97.29±0.04	97.75
6	1	0	76.09±0.74	76.02	76.52±0.00	74.81
7	-1	1	82.57±0.68	82.05	99.91±0.02	98.46
8	0	1	91.89±0.04	92.42	99.28±0.05	100.71
9	1	1	88.29±0.47	88.29	83.25±0.59	83.28

Table 4.2 Observed and predicted values of full factorial design for % As(III) and As(V) removal with Aluminum sulfate ([As] = 90 mg L^{-1})

run	coded		Aluminum sulfate			
	X_1	X_2	%As(III) removal		%As(V) removal	
			Observed	Predicted	Observed	Predicted
1	-1	-1	4.02±0.52	3.70	64.08±0.58	64.99
2	0	-1	10.03±0.20	11.18	69.79±0.44	69.74
3	1	-1	7.70±0.80	6.88	34.64±1.75	33.78
4	-1	0	4.87±1.27	4.48	85.71±0.94	85.20
5	0	0	13.62±0.23	13.38	97.79±0.04	95.30
6	1	0	9.88±0.55	10.50	61.67±0.61	64.68
7	-1	1	3.71±0.38	4.41	86.94±0.84	86.55
8	0	1	15.64±0.32	14.73	99.45±0.07	102.00
9	1	1	13.05±0.33	13.26	78.88±1.42	76.73

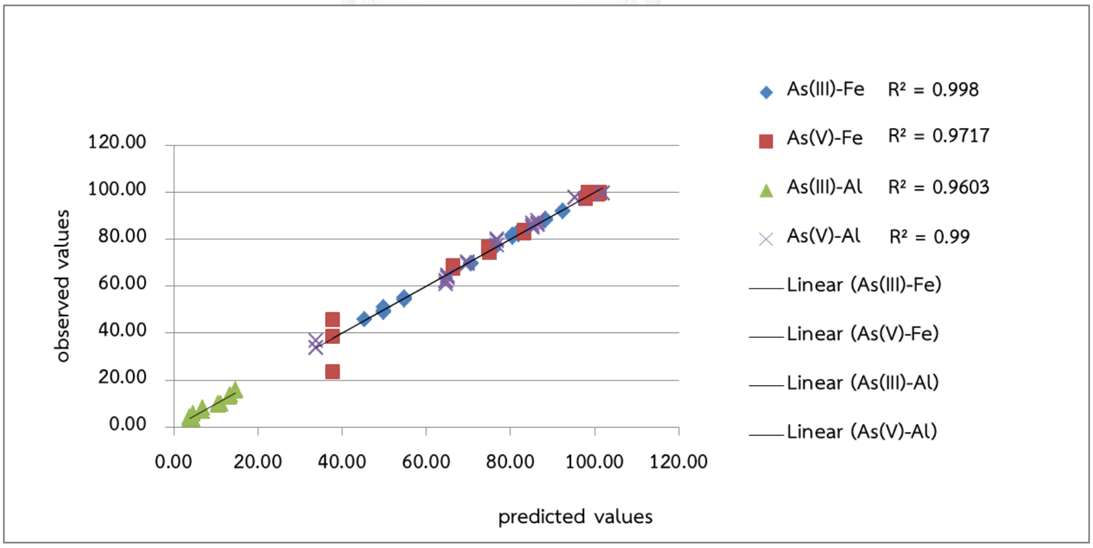


Figure 4.3 Correlation between observed values (y) and predicted values (x) for precipitation of arsenic using ferric chloride and aluminum sulfate

4.2.2 Statistical analysis

To evaluate the significance of the effects (parameters) on the process, analysis of variance (ANOVA) was calculated. The calculation of each value in ANOVA table is shown in Section 2.3.5. The results of ANOVA calculations through *F*-statistics and *p*-values for the quadratic models of As(III) and As(V) are shown in Tables 4.2-4.5. High *F*-values and low pure errors are considered as required fit criteria for an applicable model. In the study, the model with *F*-values of 2061.71, 144.34, 101.68 and 416.43 for precipitation of As(III) and As(V) using ferric chloride and aluminum sulfate, respectively, implies significance with only <0.01% chance that the large model *F*-value could occur due to noise. The model parameters are predicted to be significant for *p-value* less than 0.01, while greater than 0.01 are not significant. The significant model parameters for both arsenic species are indicated in Tables 4.3-4.5, highlighted by a superscripted " ^{s} " symbol. From the ANOVA test, it is evident that the linear parameters of pH (X_1) and concentration of co-precipitant (X_2) are significant with small *p*-values (< 0.0001) for both As(III) and As(V) removal. This denotes that the chosen factors have high proportionality in relation to the removal efficiency, and that the domain of the chosen factors is reasonable to be used for an approximation of the regression model. Comparing a significant relationship of each effect (parameter) on the response, the amount of co-precipitant is more significant than the pH effect with higher *SS* and *F*-values for all designs. The interactive terms are significant except for As(III)-Fe design.

Table 4.3 ANOVA table for As(III) removal using ferric chloride for the full factorial design

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	7095.13	5	1419.03	2061.71	<0.0001 ^{s}
X_1 (pH)	134.18	1	134.18	194.96	<0.0001 ^{s}
X_2 (Fe)	6356.73	1	6356.73	9235.73	<0.0001 ^{s}
X_1^2	315.70	1	315.70	458.68	<0.0001 ^{s}
X_2^2	286.71	1	286.71	416.56	<0.0001 ^{s}
X_1X_2	1.82	1	1.82	2.64	0.1191
Residual	14.45	21	0.69		
Lack of fit	7.82	3	2.61	7.08	0.0257
pure error	6.63	18	0.37		
Cor total	7109.59	26			

Table 4.4 ANOVA table for As(V) removal using ferric chloride for the full factorial design

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	10603.83	5	2120.77	144.34	<0.0001 ^{s}
X_1 (pH)	3091.05	1	3091.05	210.38	<0.0001 ^{s}
X_2 (Fe)	5344.09	1	5344.09	363.73	<0.0001 ^{s}
X_1^2	580.61	1	580.61	39.52	<0.0001 ^{s}
X_2^2	1223.21	1	1223.21	83.25	<0.0001 ^{s}
X_1X_2	364.88	1	364.88	24.83	<0.0001 ^{s}
Residual	308.54	21	14.69		
Lack of fit	271.04	3	90.35	43.36	0.00361 ^{s}
pure error	37.50	18	2.08		
Cor total	10912.38	26			

Table 4.5 ANOVA table for As(III) removal using aluminum sulfate for the full factorial design

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	452.90	5.00	90.58	101.68	<0.0001 ^{s}
X_1 (pH)	162.66	1	162.66	182.60	<0.0001 ^{s}
X_2 (Al)	56.70	1	56.70	63.65	<0.0001 ^{s}
X_1^2	208.38	1	208.38	233.92	<0.0001 ^{s}
X_2^2	1.10	1	1.10	1.23	0.279662989
X_1X_2	24.06	1	24.06	27.01	<0.0001 ^{s}
Residual	18.71	21	0.89		
Lack of fit	12.16	3	4.05	11.15	0.013135816
pure error	6.54	18	0.36		
Cor total	471.61	26			

Table 4.6 ANOVA table for As(V) removal using aluminum sulfate for the full factorial design

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	9937.49	5	1987.50	416.43	$<0.0001^{s}$
X_1 (pH)	1893.49	1	1893.49	396.73	$<0.0001^{s}$
X_2 (Al)	4681.49	1	4681.49	980.89	$<0.0001^{s}$
X_1^2	2486.40	1	2486.40	520.96	$<0.0001^{s}$
X_2^2	533.20	1	533.20	111.72	$<0.0001^{s}$
X_1X_2	342.90	1	342.90	71.85	$<0.0001^{s}$
Residual	100.23	21	4.77		
Lack of fit	85.10	3	28.37	33.75	0.0042358^{s}
pure error	15.13	18	0.84		
Cor total	10037.71	26			

4.2.3 Effect of solution pH and co-precipitant concentration on arsenic removal

According to Figure 4.4, the efficiency of As(III) removal using ferric chloride increases with increasing pH from 5 to 9 because negatively charge of $H_2AsO_3^-$ is predominant in solution [2] inducing more precipitates. Conversely, the efficiency of As(V), as shown in Figure. 4.5 and 4.7, increases when decreasing pH from 9 to 5 because negatively charged $H_2AsO_4^-$ [2] can be precipitated with cations of ferric ions [32] and aluminum ions. For co-precipitant concentration effect, when a ratio of co-precipitant/As increases, the efficiency of arsenic removal will be higher [7].

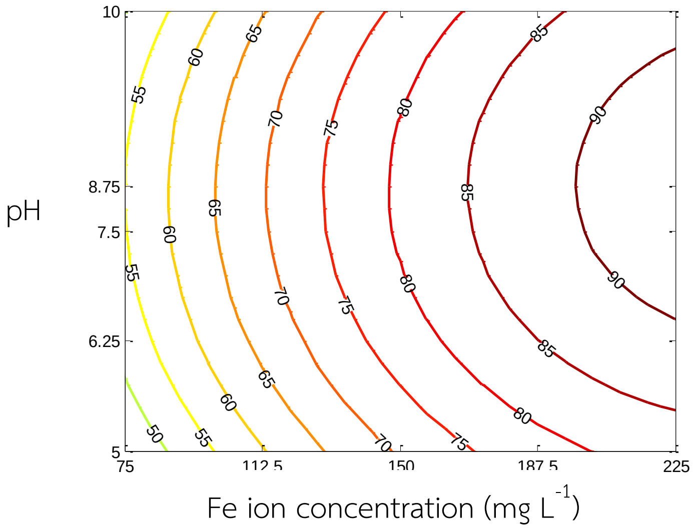


Figure 4.4 Contour plot of As(III) removal efficiency using ferric chloride

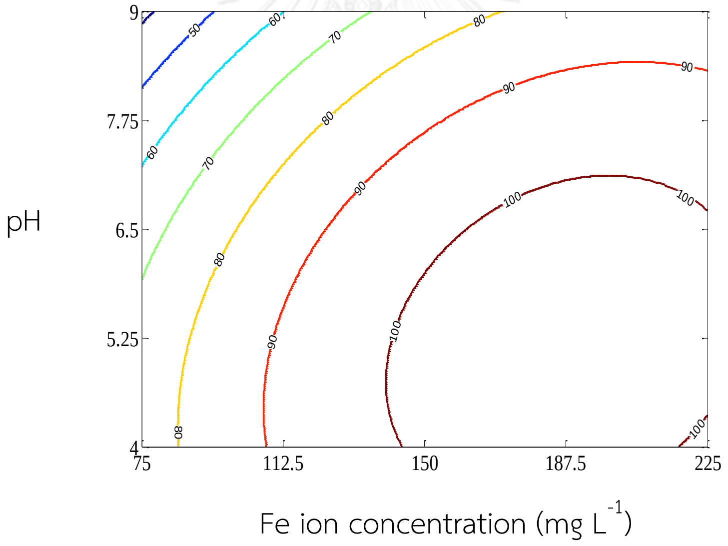


Figure 4.5 Contour plot of As(III) removal efficiency using ferric chloride

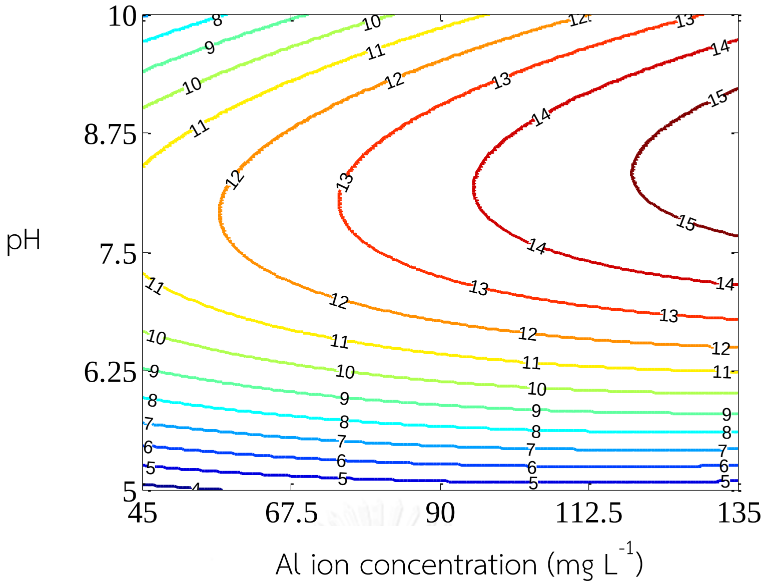


Figure 4.6 Contour plot of As(III) removal efficiency using aluminum sulfate

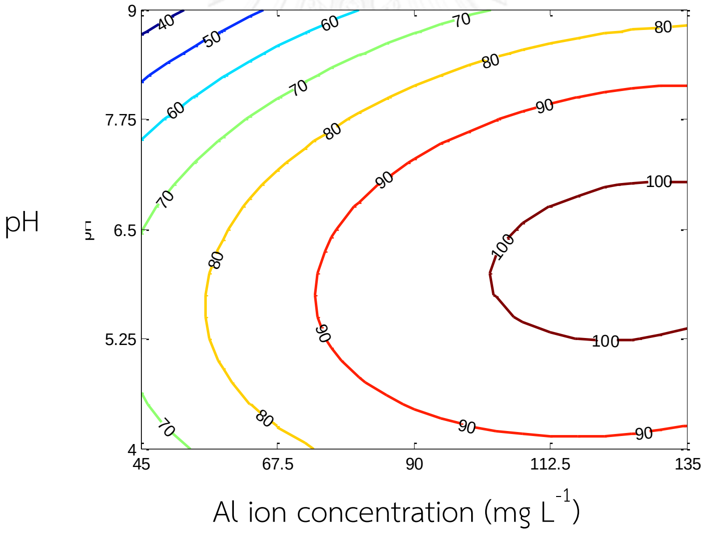


Figure 4.7 Contour plot of As(V) removal efficiency using aluminum sulfate

4.3 Central composite designs

In Section 4.2, aluminum sulfate cannot be an effective co-precipitant for As(III) removal although the ratio of aluminum sulfate/As(III) increases. Therefore, the central composite designs (CCD) for precipitating As(III) and As(V) using ferric chloride and precipitating As(V) using only aluminum sulfate were studied.

For the construction of the design, the factors of each level were constructed which were shown in Table 3.12, 3.14 and 3.16 for the precipitation of As(III) and As(V) with ferric chloride and the precipitation of As(V) with aluminum sulfate, respectively. The evaluating ranges of pH for the precipitation of As(III) and As(V) is the same as that of the full factorial design.

4.3.1 Regression models

A regression model including quadratic parameters correlating the arsenic removal efficiency with interactive parameters was calculated though Multiple Linear Regression (MLR). The proposed constructed function has ten parameters consisting of one constant effect (intercept), three primary effects, three curvature effects and three two-factor interaction effects. After performing MLR to obtain the parameter coefficients, the following quadratic regression model shown in Equations (4.5)-(4.7) for the precipitation of As(III) and As(V) using ferric chloride and the precipitation of As(V) using aluminum sulfate, respectively, calculated using coded values, can be used to express the removal efficiency of As(III) and As(V), respectively.

$$\begin{aligned}\text{\%As(III) removal} = {} & 81.65+1.53X_1+18.51X_2-10.40X_3-1.89X_1^2-8.09X_2^2-0.97X_3^2 \\ & +0.02X_1X_2+0.20X_1X_3+2.97X_2X_3\end{aligned} \tag{4.5}$$

$$\begin{aligned}\text{\%As(V) removal} = {} & 94.06-5.32X_1+17.15X_2-11.62X_3-0.96X_1^2-10.07X_2^2-2.66X_3^2 \\ & +1.03X_1X_2-0.29X_1X_3+10.06X_2X_3\end{aligned} \tag{4.6}$$

$$\begin{aligned}\text{\%As(V) removal} = {} & 96.86-7.93X_1+16.06X_2-9.13X_3-4.29X_1^2-10.39X_2^2-1.29X_3^2 \\ & +2.06X_1X_2-1.13X_1X_3+7.58X_2X_3\end{aligned} \tag{4.7}$$

The sign of the coefficient in the regression function indicates the direction of influence of the parameter on the response. A positive effect for a factor indicates that the response is enhanced when the parameter level increases, and a negative effect shows that the response is reduced when the factor level increases. The intensity of the sign effect is denoted by the magnitude of the coefficient. Basically, parameters that are demonstrably larger in magnitude will have greater significance compared with small magnitude parameters. Interestingly, the opposite coefficient signs of X_1 factor (solution pH) which is positive for As(III) and negative for As(V) were noticed (Equations (4.5)–(4.7)) This suggests that monovalent anions ($H_2AsO_3^-$ and $H_2AsO_4^-$) are preferred in the co-precipitation process. For As(III), when the pH is increased from 7 to 10, the relative fraction of $H_2AsO_3^-$ increases, meanwhile in case of As(V), when the pH is lowered from 9 to 4, the fraction of $H_2AsO_4^-$ increases [2] This observation was in agreement with experimental results reported by Meng et al. [32]. Thus in this case, a "One-factor at a time" method is not satisfactory for simultaneous removal of As(III) and As(V) because the solution pH could affect on species distribution of arsenic. It means that the form of arsenic can differ upon pH change. Therefore it is necessary to apply the RSM approach.

The determination of the correlation coefficients (R^2), which are obtained from the regression model show a satisfied quality of fit of 0.9871, 0.9478 for As(III) and As(V) removal using ferric chloride and 0.9153 for As(V) removal using aluminum sulfate (Figure 4.8). We again refer to this step as the model calibration. The results indicate that the model provides a sufficient representation of the real relationship among these variables. The accumulation of the points around the fitted line indicates a satisfactory correlation between the experimental data and the predicted values, demonstrating that the regression models are appropriate for predicting the response.

Table 4.7 Observed and predicted values of the CCD for % As(III) removal with ferric chloride

run	pH (X_1)		Fe conc. (mg/L) (X_2)		Initial As conc.(mg/L)(X_3)		%As removal	
	actual	code	actual	code	actual	code	observed	predicted
1	6	-1	75	-1	45	-1	63.33±0.71	64.26
2	9	1	75	1	45	-1	70.30±0.32	66.86
3	6	-1	225	-1	45	-1	92.92±0.21	95.29
4	9	1	225	1	45	-1	96.73±0.11	98.00
5	6	-1	75	-1	135	1	37.73±0.48	37.10
6	9	1	75	1	135	1	42.25±0.36	40.52
7	6	-1	225	-1	135	1	75.95±0.30	80.02
8	9	1	225	1	135	1	83.82±0.17	83.54
9	7.5	0	150	0	90	0	81.58±0.42	81.65
10	7.5	0	23.85	-1.68	90	0	24.41±0.60	27.62
11	7.5	0	276	1.68	90	0	93.99±0.09	89.89
12	7.5	0	150	0	167.27	1.68	61.94±0.10	61.40
13	7.5	0	150	0	14.55	-1.68	96.75±0.76	96.40
14	5	-1.68	150	0	90	0	77.43±0.45	73.73
15	10	1.68	150	0	90	0	76.09±0.74	78.89

Table 4.8 Observed and predicted values of the CCD for % As(V) removal with ferric chloride

run	pH(X_1)		Fe conc. (mg/L) (X_2)		Initial As conc.(mg/L)(X_3)		%As removal	
	actual	code	actual	code	actual	code	observed	predicted
1	5	-1	75	-1	45	-1	99.07±0.10	90.95
2	8	1	75	-1	45	-1	84.76±0.42	78.84
3	5	-1	225	1	45	-1	99.90±0.00	103.08
4	8	1	225	1	45	-1	98.60±0.03	95.08
5	5	-1	75	-1	135	1	49.17±0.97	48.18
6	8	1	75	-1	135	1	42.58±1.98	34.89
7	5	-1	225	1	135	1	99.14±0.23	100.55
8	8	1	225	1	135	1	87.76±0.20	91.37
9	6.5	0	150	0	90	0	94.60±2.97	94.06
10	6.5	0	23.85	-1.68	90	0	25.39±0.66	36.72
11	6.5	0	276	1.68	90	0	99.38±0.03	94.42
12	6.5	0	150	0	167.27	1.68	66.99±0.49	66.99
13	6.5	0	150	0	14.55	-1.68	99.72±0.10	106.08
14	4	1.68	150	0	90	0	99.78±0.05	100.29
15	9	1.68	150	0	90	0	76.52±1.45	82.39

Table 4.9 Observed and predicted values of the CCD for %As(V) removal with aluminum sulfate

run	pH (X_1)		Fe conc. (mg/L) (X_2)		Initial As conc.(mg/L)(X_3)		%As removal	
	actual	code	actual	code	actual	code	observed	predicted
1	5	-1	45	-1	45	-1	98.53±0.08	90.39
2	7.9	1	45	-1	45	-1	81.70±0.65	72.67
3	5	-1	135	1	45	-1	99.84±0.02	103.23
4	7.9	1	135	1	45	-1	99.09±0.17	93.76
5	5	-1	45	-1	135	1	59.56±1.06	59.25
6	7.9	1	45	-1	135	1	46.04±1.47	37.00
7	5	-1	135	1	135	1	99.00±0.27	102.39
8	7.9	1	135	1	135	1	85.90±0.24	88.39
9	6.5	0	90	0	90	0	97.54±0.28	96.86
10	6.5	0	14	-1.68	90	0	27.42±1.26	40.46
11	6.5	0	167	1.68	90	0	99.53±0.05	94.48
12	6.5	0	90	0	167.27	1.68	78.50±0.69	77.84
13	6.5	0	90	0	14.55	-1.68	99.91±0.06	108.55
14	4	-1.68	90	0	90	0	99.78±0.05	98.05
15	9	1.68	90	0	90	0	61.67±0.61	71.38

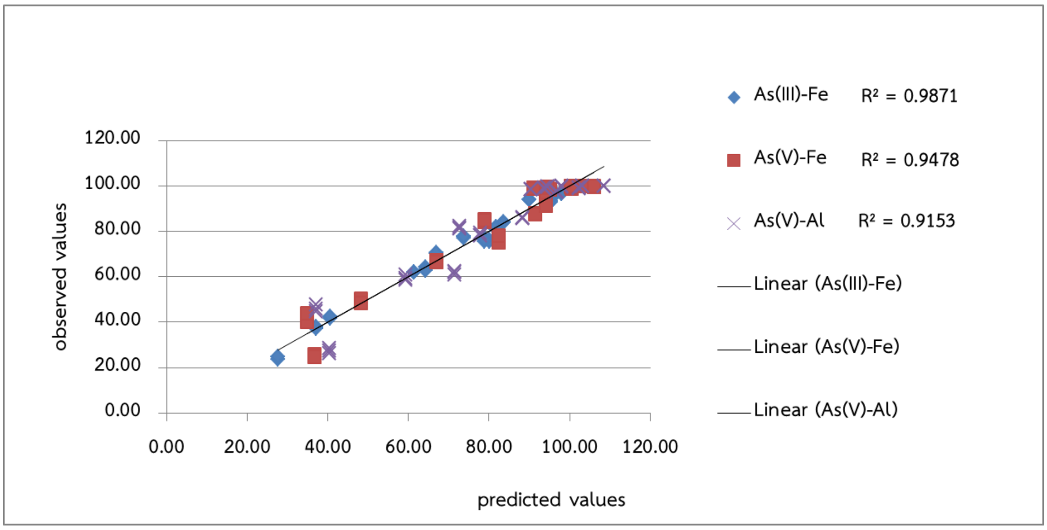


Figure 4.8 Correlation between observed values (y) and predicted values (x) of the CCD for precipitation arsenic using ferric chloride and aluminum sulfate

The regression model was generated and calibrated using the experimental points in the domain, as listed in Tables 3.12, 3.14 and 3.16. However, there is no guarantee that the model can be used to predict correctly the response of experiments undertaken using different conditions. A validation protocol is therefore necessary to describe the generality of the model, and to prevent errors from over fitting. This protocol is required prior to producing the response surface in order to determine the real optimized conditions, as it shows the ability to reproduce the system in either different laboratories or under different experimental circumstances. In this case, the regression model was validated by using the nine extra experiments, with 3 replicates in each experiment generating 27 total runs. The experimental conditions were randomly chosen within the range of the experimental domain (Table 3.12, 3.14 and 3.16) but not using the same points in the calibration set. Table S1-S3 in the appendix highlights the experimental conditions and the corresponding responses of the validation set for As(III), As(V) using ferric chloride and for As(V) using aluminum sulfate, with the correlation plot of the predicted and observed arsenic removal percentages being shown in Figure 4.9. From this, the correlation coefficients (R^2) are 0.9019 and 0.9853 for the removal of As(III) and As(V) using ferric chloride and 0.9243 for the removal of As(V) using aluminum sulfate, respectively, indicating that the R^2 is improved for As(V) and slightly decreased for As(III). However, the good correlation between predicted and observed response, especially for the external validation set, suggests that the obtained regression function (Equations 4.5-4.7) does not suffer from overfitting and can be applied to the derivation of optimized conditions for the recovery of As(III) and As(V).

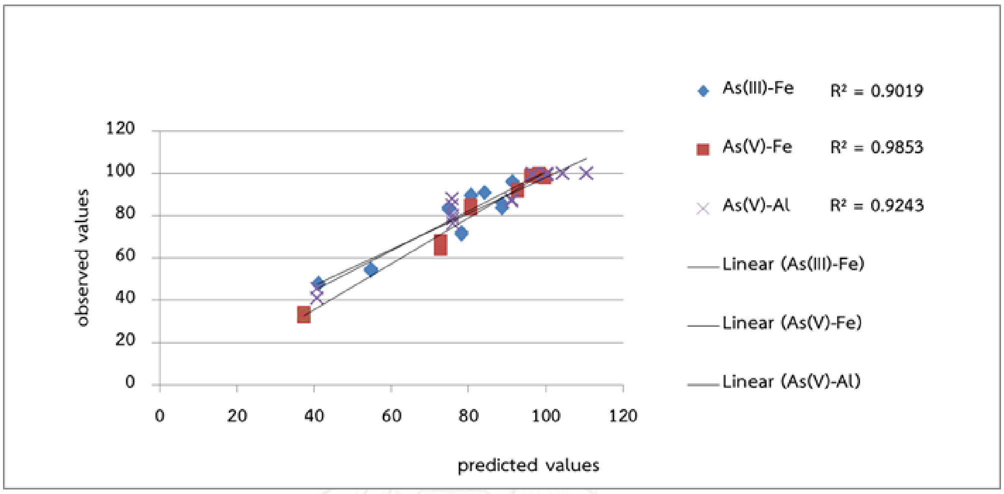


Figure 4.9 Correlation between observed values (y) and predicted values (x) of the CCD for precipitation of arsenic using ferric chloride and aluminum sulfate for model validation.

4.3.2 Statistical analysis

To evaluate the significance of the effects (parameters) on the process, analysis of variance (ANOVA) was calculated. The results of ANOVA calculations through *F*-statistics and *p*-values for the quadratic models of As(III) and As(V) removal using ferric chloride and As(V) removal using aluminum sulfate, are shown in Tables 4.10-4.11, respectively. High *F*-values and low pure errors are considered as required fit criteria for an applicable model. In the study, the model with *F*-values of 321.88 and 76.73 for As(III) and As(V) removal using ferric chloride and 45.63 for As(V) removal using aluminum sulfate, implies significance with only <0.01% chance that the large model *F*-value could occur due to noise. The model parameters are predicted to be significant for *p-value* less than 0.01, while greater than 0.01 are not significant. The significant model parameters for both arsenic species are indicated in Tables 4.10-4.11, highlighted by a superscripted “^{S} ” symbol. From the ANOVA test, it is evident that the linear parameters of pH (X_1), concentration of ferric ion (X_2) and initial concentration of arsenic species (X_3) are significant with small *p*-values (< 0.0001) for both As(III) and As(V) removal. This denotes that the chosen factors have high proportionality in relation to the removal efficiency, and that the domain of the chosen factors is reasonable to be used for an approximation of the regression model. In fact, the factor pH plays an important role in the system as mentioned earlier. Only the quadratic parameter for concentration of co-precipitant is significant for the removal of arsenic species. If the sign and significant effect of parameter ($X_{\ 2}$) are considered ($b_2 > 0$ and $b_{22} < 0$), this indicates that there is an optimized point of X_2 in the experimental domain giving the highest removal efficiency. As seen by the co-precipitation mechanism in Section 2.2.5, the higher the molar ratio of ferric ions to other components, the greater the removal efficiency. Additionally, it should be noted that only interaction effect (X_2 X_3) was shown to significantly affect the response, as indicated by the *p*-value (< 0.0001). This observation is substantiated by the fact that a higher molar ratio of Fe/As facilitates the co-precipitation process [7].

Table 4.10 ANOVA table of the CCD for As(III) removal using ferric chloride

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	20831.91	9	2314.66	321.98	<0.0001 ^{s}
X_1 (pH)	96.22	1	96.22	13.38	0.0008 ^{s}
X_2 (Fe)	14042.32	1	14042.32	1953.33	<0.0001 ^{s}
X_3 (As)	4435.23	1	4435.23	616.95	<0.0001 ^{s}
X_1^2	132.07	1	132.07	18.37	0.0001 ^{s}
X_2^2	2427.03	1	2427.03	337.61	<0.0001 ^{s}
X_3^2	35.16	1	35.16	4.89	0.0331
X_1X_2	0.01	1	0.01	0.00	0.9643
X_1X_3	0.99	1	0.99	0.14	0.7125
X_2X_3	211.92	1	211.92	29.48	<0.0001 ^{s}
Residual	273.18	38	7.19		
Lack of fit	266.87	5	53.37	29.02	0.0001 ^{s}
pure error	6.31	33	0.19		
Cor total	21105.09	47			

Table 4.11 ANOVA table of the CCD for As(V) removal using ferric chloride

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	24400.34	9	2711.15	76.73	<0.0001 s
X_1 (pH)	1160.53	1	1160.53	32.85	<0.0001 s
X_2 (Fe)	12054.13	1	12054.13	341.17	<0.0001 s
X_3 (As)	5533.66	1	5533.66	156.62	<0.0001 s
X_1^2	34.26	1	34.26	0.97	0.3310
X_2^2	3755.95	1	3755.95	106.30	<0.0001 s
X_3^2	261.72	1	261.72	7.41	0.0097 s
X_1X_2	25.35	1	25.35	0.72	0.4023
X_1X_3	2.06	1	2.06	0.06	0.8103
X_2X_3	2428.99	1	2428.99	68.75	<0.0001 s
Residual	1342.61	38	35.33		
Lack of fit	1305.11	5	261.02	229.06	0.0001 s
pure error	37.50	33	1.14		
Cor total	25742.95	47			

Table 4.12 ANOVA table of the CCD for As(V) removal using aluminum sulfate

source	Sum of squares	*df*	Mean square	*F* value	*p* value prob > *F*
model	21408.33	9	2378.70	45.63	<0.0001 ^{s}
X_1 (pH)	2575.85	1	2575.85	49.42	<0.0001 ^{s}
X_2 (Al)	10562.97	1	10562.97	202.64	<0.0001 ^{s}
X_3 (As)	3414.20	1	3414.20	65.50	<0.0001 ^{s}
X_1^2	681.88	1	681.88	13.08	0.0009 ^{s}
X_2^2	3996.71	1	3996.71	76.67	<0.0001 ^{s}
X_3^2	61.98	1	61.98	1.19	0.2824
X_1X_2	102.02	1	102.02	1.96	0.1699
X_1X_3	30.70	1	30.70	0.59	0.4476
X_2X_3	1377.18	1	1377.18	26.42	<0.0001 ^{s}
Residual	1980.77	38	52.13		
Lack of fit	1967.96	5	393.59	1013.64	0.0001 ^{s}
pure error	12.82	33	0.39		
Cor total	23389.10	47			

4.3.3 Effect of pH solution, co-precipitant and initial arsenic concentration on arsenic removal

4.3.3.1 The response surface for co-precipitation of As(III) and As(V) using ferric chloride

The response surface is a collection of the responses calculated from the statistical/mathematical model that are used for analyzing the process. The main objective of the RSM method is to optimize the response surface, as influenced by various factors, and to quantify the relationship between the controllable input parameters and the corresponding response surfaces. To have a better illustration of the results and to understand the relationships between the major factors, three-dimensional response surface plots of the As(III) and As(V) removal percentages are presented in Figure 4.10 and 4.14, respectively. Generally, the axes in the surface plot can be selected as interaction statements having the largest absolute coefficients in the model, and p-values < 0.01. In our case, only the interaction of X_2 X_3 is significant from the ANOVA test. Plotting the surface response using the interaction of factors X_2 and X_3 might not provide an adequate interpretation as the individual factor X_1 (pH) is also significant and, interestingly, opposite signs for the parameter coefficient are observed for As(III) and As(V). Moreover, the initial arsenic concentrations may vary in different applications. Therefore, we attempt to present all interactions in one surface plot by setting the x- and y-axis to be X_1 (pH) and X_2 (ferric ion concentration), respectively, together with the surface layers corresponding to the different initial arsenic concentrations being superimposed in order to include all interactions of factors X_1, X_2 and X_3. Figure 4.10 and 4.14 show that the removal efficiency increases on increasing the co-precipitant concentration, while it remains unchanged at different pH values. However, the recovery efficiency varies dramatically with initial arsenic concentration, especially for the removal process of As(V). From the superimposed surface plots, it can be noted that the removal efficiency decreases as the initial arsenic concentration is increased. This is in good agreement with the regression functions (Equations 4.5-4.6) where a negative sign for factor X_3 was observed in both removal processes. Consequently, the highest removal percentage will be found when the initial arsenic concentration is lowest.

The effect of pH and ferric ions concentrations on As(III) removal is shown in Figure 4.11. The maximum efficiency is 90 % of As(III) removal in the pH range of 6.5–9.5 and the ferric ions concentrations of 190-276 mg L^{-1}. At pH more than 9.5, the efficiency decreased because ferric hydroxide is more negatively charged on surface at high pH.

The effect of pH and initial As(III) concentrations on As(III) removal at a fixed ferric ions concentrations of 150 mg L^{-1} is shown in Figure 4.12. The maximum efficiency is 95% of As(III) removal at the pH higher than 6 and the initial As(III) concentration is approximately less than 16 mg L^{-1}.

The effect of ferric ion concentration and initial As(III) concentrations on As(III) removal at pH 7.5 is shown in Figure 4.13. The efficiency increases when the ratio of Fe/As(III) is increased. The maximum efficiency is around 100 % of As(III) removal in the range of ferric ions concentrations between 150-250 mg L^{-1} and the initial As(III) concentration is approximately less than 35 mg L^{-1}.

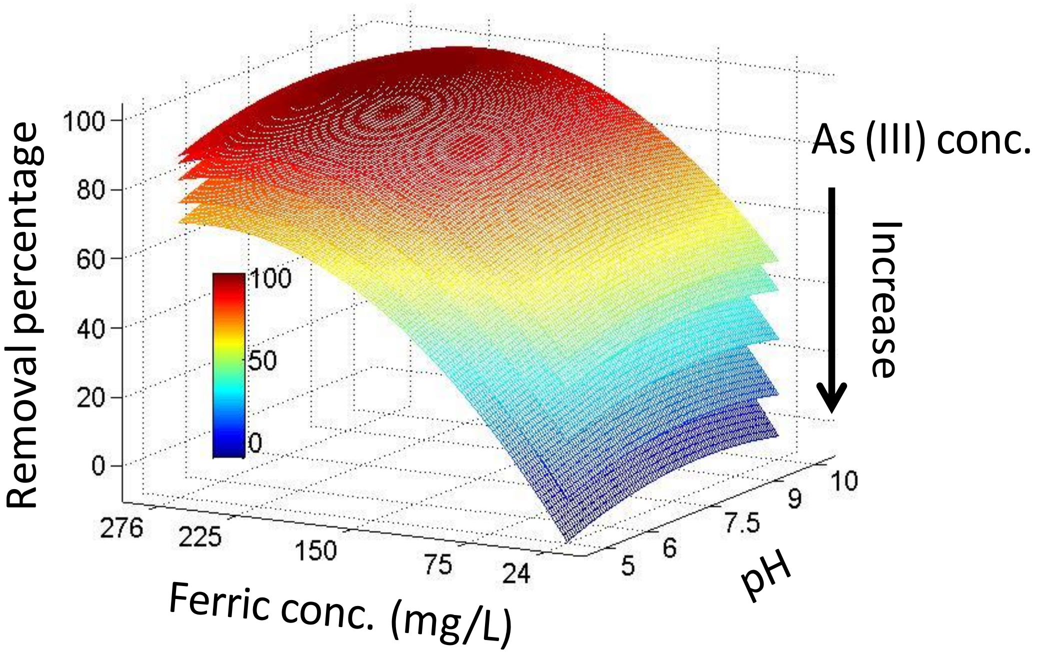


Figure 4.10 Combined effect of pH and amount of ferric chloride on As(III) removal at each level of initial As(III) concentration.

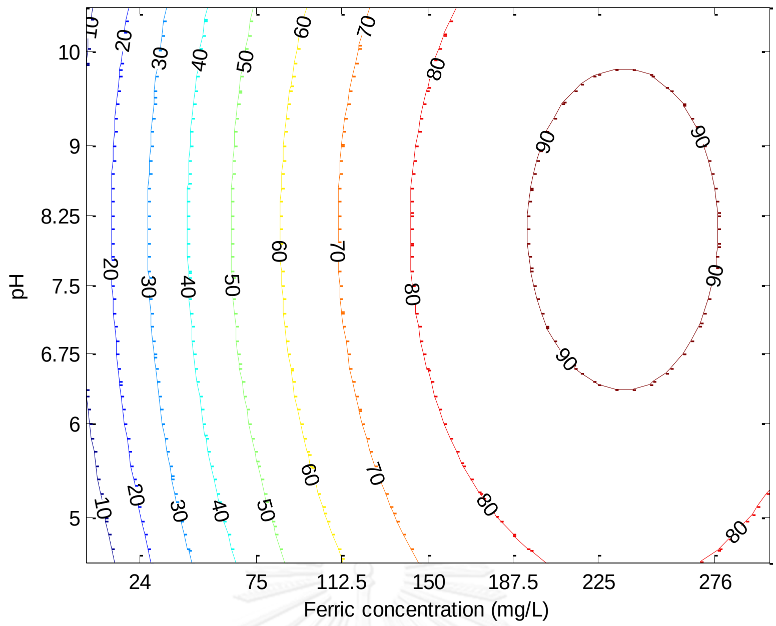


Figure 4.11 Contour plot show interaction pH and Ferric ions concentrations (mg L^{-1}) on removal efficiency of As(III) at initial As(III) concentration of 90 mg L^{-1}.

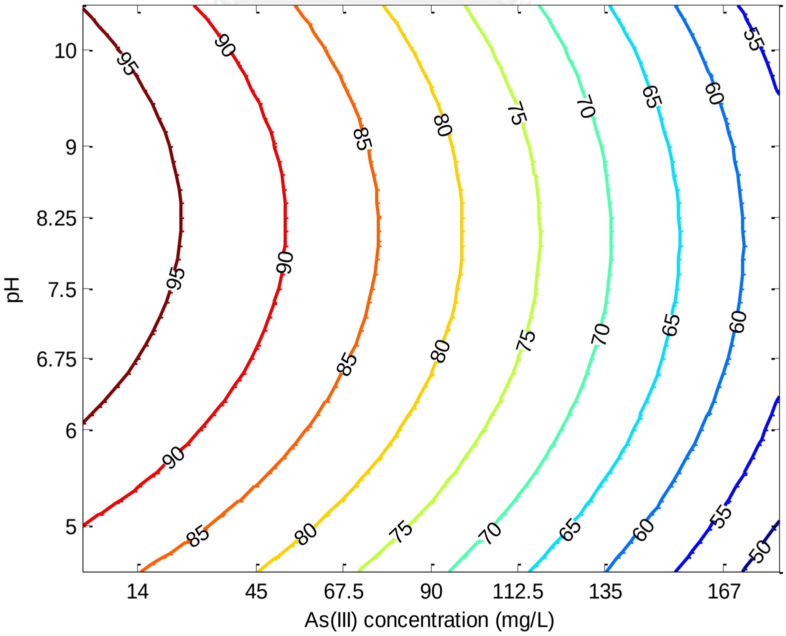


Figure 4.12 Contour plot show interaction pH and As concentration (mg L^{-1}) on removal efficiency of As(III) at ferric ion concentration of 150 mg L^{-1}.

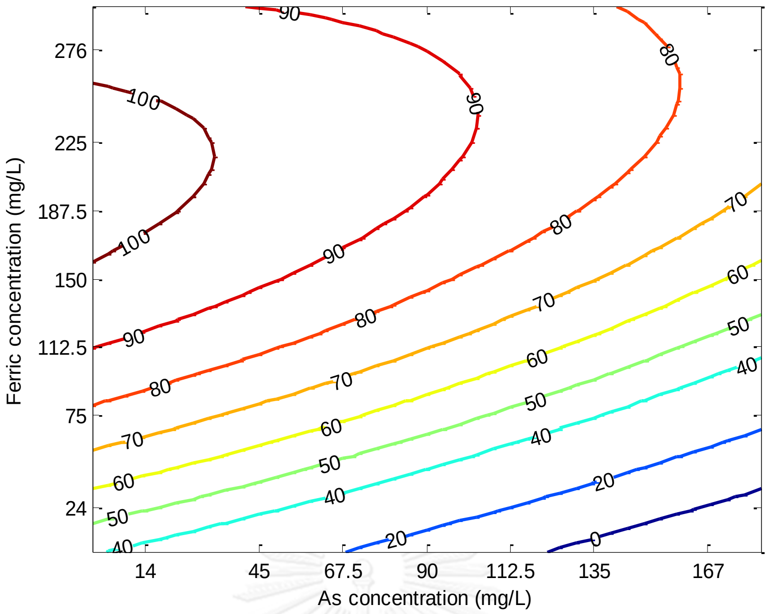


Figure 4.13 Contour plot show interaction Ferric ion concentration (mg L^{-1}) and As concentration (mg L^{-1}) on removal efficiency of As(III) at pH of 7.5.

The effect of pH and ferric ion concentrations on As(V) removal is shown in Figure 4.15. The maximum efficiency is 100 % of As(V) removal at the pH less than 6.5 and the ferric ion concentration is above 150 mg L^{-1}.

The effect of pH and initial As(V) concentrations on As(V) removal at a fixed ferric ion concentration of 150 mg L^{-1} is shown in Figure 4.16. The maximum efficiency is 100 % of As(V) removal at the pH less than 6 and the initial As(III) concentration is approximately less than 90 mg L^{-1}.

For the effect of ferric ion concentration and initial As(V) concentration on As(V) removal at pH 6.5, the simulated result is shown in Figure 4.17. The efficiency increases when the ratio of Fe/As(V) is increased. The maximum efficiency is 100 % of As(V) removal when the range of ferric ion concentration is between 75-200 mg L^{-1} with depending on the level of the initial As(V) concentration which is shown in Figure 4.17.

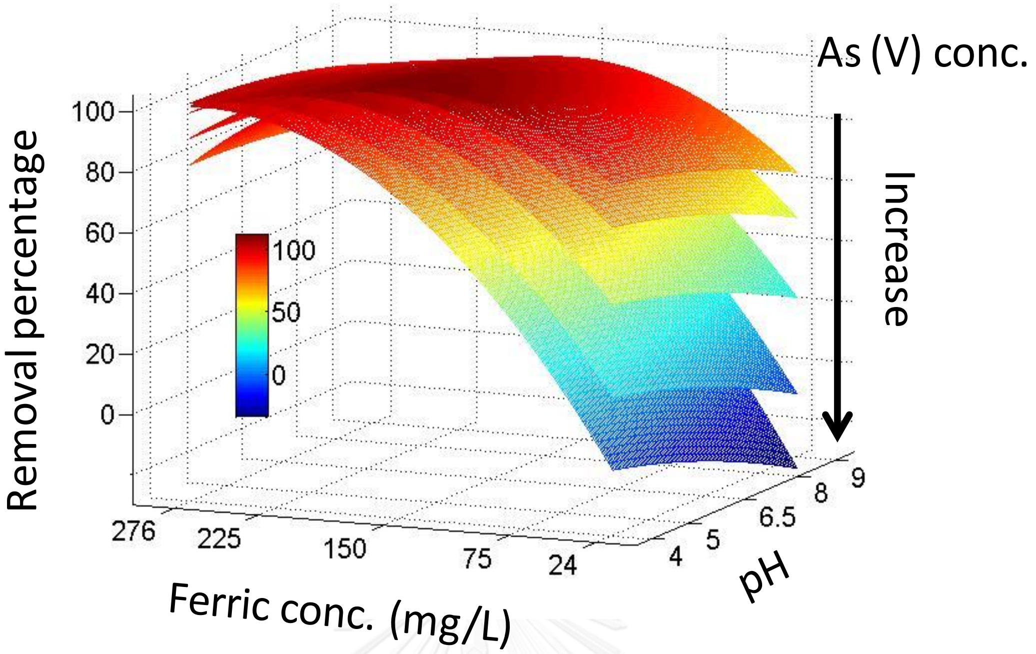


Figure 4.14 combined effect of pH and amount of ferric chloride on As(V) removal at each level of initial As(V) concentration.

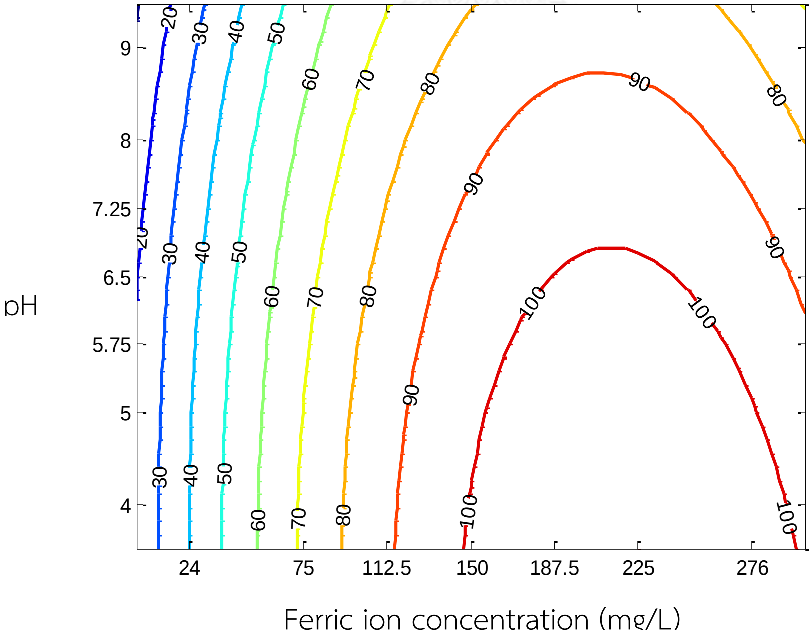


Figure 4.15 Contour plot show interaction pH and Ferric ion concentration (mg L^{-1}) on removal efficiency of As(V) at initial As(V) concentration of 90 mg L^{-1}.

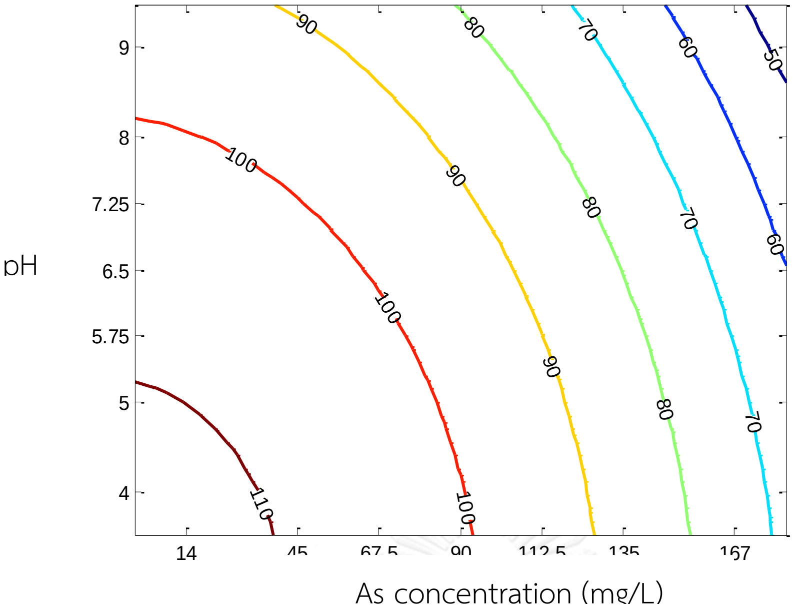


Figure 4.16 Contour plot show interaction pH and initial As(V) concentration (mg L^{-1}) on removal efficiency of As(V) at Ferric ion concentration of 150 mg L^{-1}.

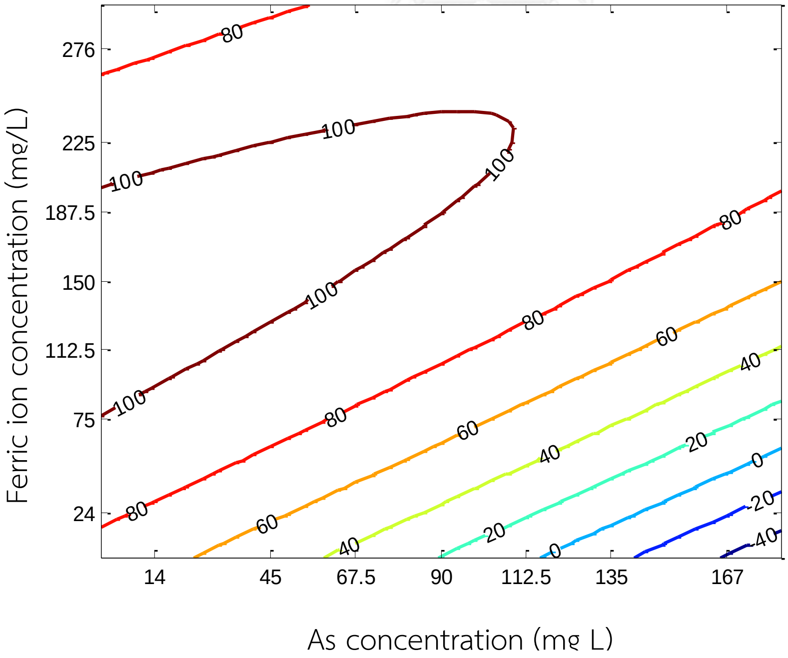


Figure 4.17 Contour plot show interaction Ferric ion concentration (mg L^{-1}) and initial As(V) concentration (mg L^{-1}) on removal efficiency of As(V) at .pH of 6.5.

4.3.3.2 Response surface for co-precipitation of As(V) using aluminum sulfate

The response surface for As(V) removal using aluminum sulfate, the interaction of 3 independent variables show the same effectiveness as As(V) removal using ferric chloride. The efficiency increases when increasing aluminum ion concentration while the initial As(V) concentration and pH solution decreased which correlate to the positive sign of coefficient terms of aluminum ion concentration as shown in Equation (4.7) while the initial As(V) concentration and pH solution correlate to the negative sign coefficient terms as shown in Equation (4.7).

$$\begin{aligned}\%\text{As(V) removal} = {} & 96.86-7.93X_1+16.06X_2-9.13X_3-4.29X_1^2-10.39X_2^2-1.29X_3^2 \\ & +2.06X_1X_2-1.13X_1X_3+7.58X_2X_3\end{aligned} \tag{4.7}$$

The effect of pH and aluminum ion concentrations on As(V) removal is shown in Figure 4.18. The maximum efficiency is 100 % of As(V) removal in the pH range 4.0-7.0 and the ferric ion concentration between 90-140 mg L^{-1}.

The effect of pH and initial As(V) concentrations on As(V) removal at a fixed aluminum ion concentration of 90 mg L^{-1} is shown in Figure 4.19. The maximum efficiency is 100 % of As(V) removal at pH less than 8 with depending on the level of initial As(V) concentration which is shown in Figure 4.19.

The effect of aluminum ion concentrations and initial As(V) concentrations on As(V) removal at pH 6.5 is shown in Figure 4.20. The efficiency increases when the ratio of Al/As(V) is increased. The maximum efficiency of As(V) removal is 100 % in the range of aluminum ion concentration between 45-135 mg L^{-1} with depending on the level of initial As(V) concentration which is shown in Figure 4.20.

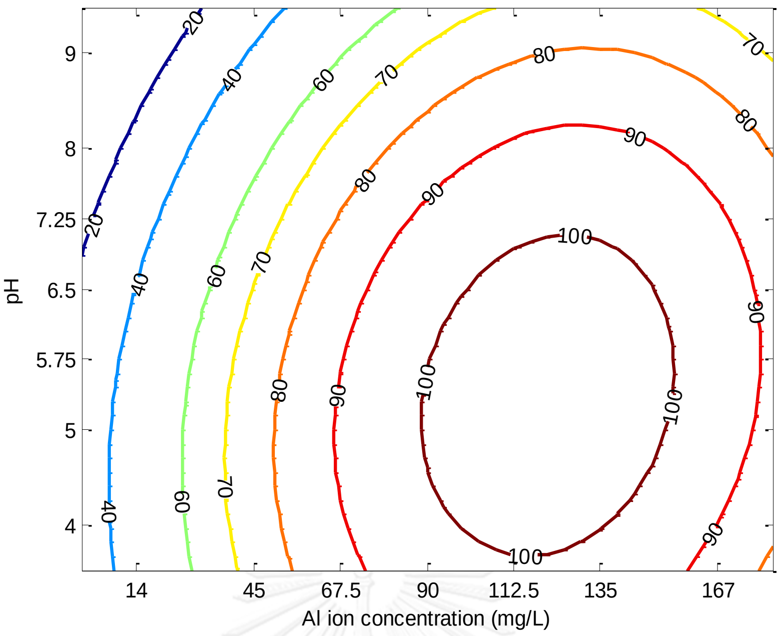


Figure 4.18 Contour plot show interaction pH and Al ion concentration (mg L^{-1}) on removal efficiency of As(V) at initial As(V) concentration of 90 mg L^{-1}.

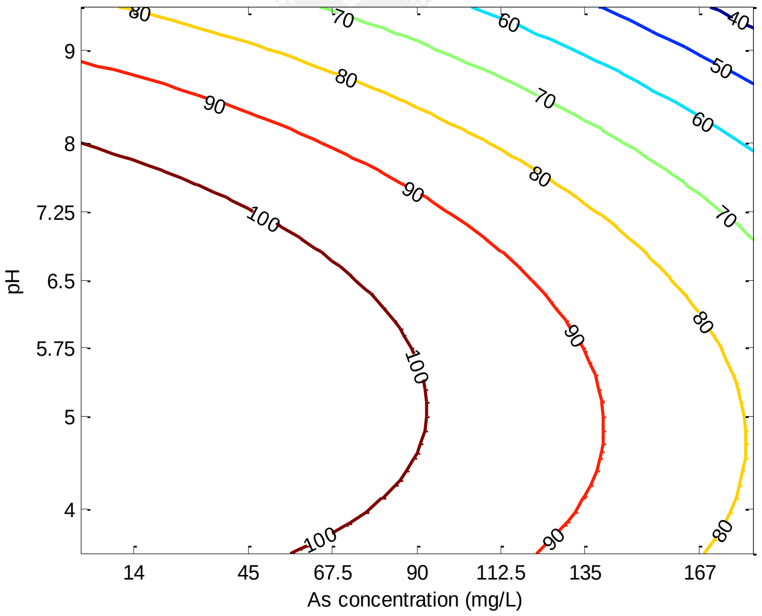


Figure 4.19 Contour plot show interaction pH and As concentration (mg L^{-1}) on removal efficiency of As(V). at Al ion concentration of 90 mg L^{-1}.

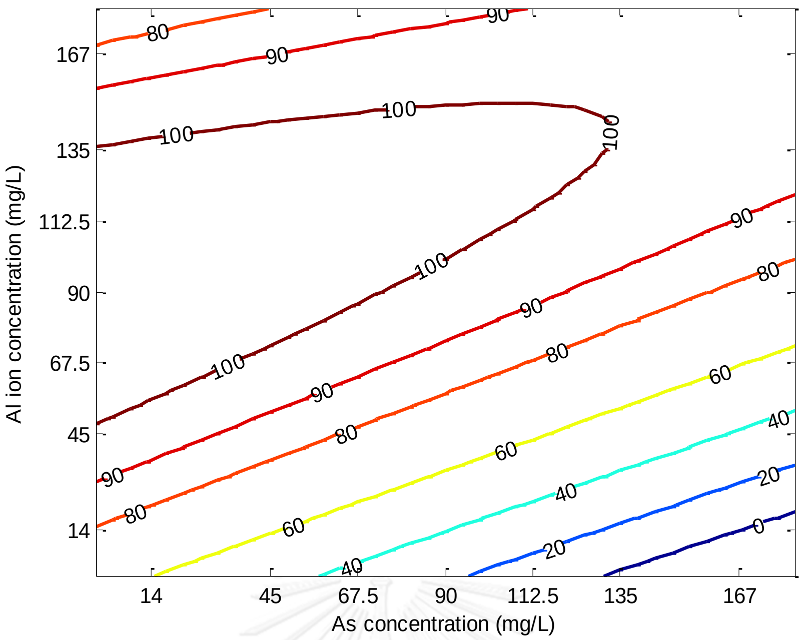


Figure 4.20 Contour plot show interaction Al ion concentration (mg L^{-1}) and As concentration (mg L^{-1}) on removal efficiency of As(V) at pH of 6.5.

4.4 Optimization

To better visualize how the optimized conditions were obtained, the superimposed contour plots of the removal percentages using the lowest initial arsenic concentration are shown in Figure 4.21. Solid, and dotted lines in the contour plot represent the responses of As(III) and As(V), respectively, and the x-axis is labeled as the solution pH range in accordance with the different pH domains in the CCD (lower bound: pH for As(V) and upper bound: pH for As(III)). A perfect removal efficiency (100%) was found at the high ferric ion concentration, and over a pH range of 6-8 for both arsenic species. The area of 100% removal efficiency for As(V) is broader than that for As(III) because As(V) can more easily attach to the surface of ferric hydroxides, as reflected by the equilibrium constants (log *K*) of surface complexes of -3.1 for As(III), and 0.6 for As(V) [32]. Optimized conditions for simultaneous removal of As(III) and As(V) were chosen from the overlapped contour area (labeled in orange).

To assess the optimized conditions of combined As(III) with As(V) in the system using aluminum sulfate, aluminum sulfate can not precipitate As(III) as well as As(V) that was discussed in the rulsult of full factorial design. Therefore, the optimized conditon was evaluted by investigating only the RSM of As(V). From the Figures 4.18-4.20, the optimized conditons were found as the pH range of 5-7 and the Al ion concentration of 135 mg L^{-1}.

In this research, the optimized pH was chosen as pH of 7 with normally pH in natural water and the amount of co-precipitants were 225 and 135 mg L^{-1} for ferric ions and aluminum ions, respectively. These opitimized conditions will be used in the Section 4.5 (Removal arsenic in mixtures and real samples). However, these optimized conditions can be used for the removal of arsenic at the concentrations lower than 45 mg L^{-1}.

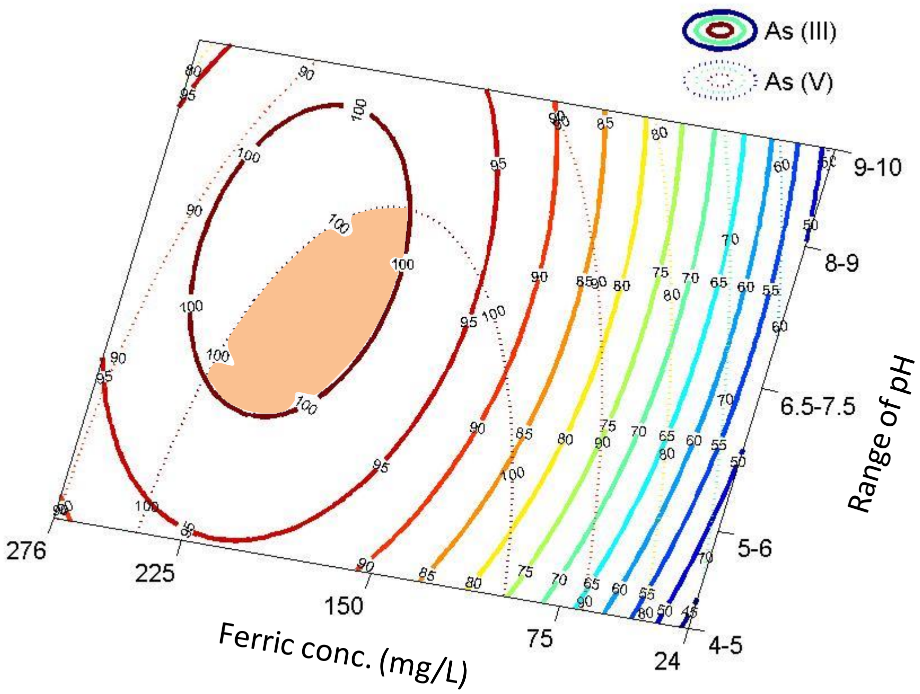


Figure 4.21 Superimposed contour plots of the arsenic removal with fixed intial arsenic concentration of the lowest level.

4.5 Removal arsenic in mixtures and real samples

According to the Figure 4.22, the maximum removal efficiency of As(III) and As(V) were predicted from the RSM method using the following conditions: pH 7 and a ferric ion concentration of 225 mg L^{-1} .As mentioned in the Section 3.7, the total concentration of arsenic in each mixture was 90 mg L^{-1} including natural water spiked with As(III) and As(V) while the total concentration of arsenic in wastewater samples is approximately 66-68 mg L^{-1}. The detail of samples is shown in Table 3.18.

Six mixtures of As(III) and As(V) at different ratios, and wastewater samples from the petroleum industry were used in order to demonstrate the efficiency and effectiveness of the removal process. Recovery percentages of the experiments, including the variations performed at the optimized condition settings, are illustrated in Figures 4.22 and 4.23. For the mixture samples, the recovery percentage of arsenic species is in range of 88% – 98% with small standard variation (error scaled bar) as calculated from three repeated runs. This indicates that the chosen conditions are promising, from the high removal efficiency and good reproducibility. Interestingly, a decrease in removal efficiency in mixtures with higher ratio of As(III) occurred, due to the low equilibrium constant for surface complex formation [32]. In case of the wastewater samples, more than 90% removal was observed using the optimized conditions, indicating the usefulness of the RSM method in the derivation of such conditions, and outlining the potential of co-precipitation as a low cost, environmentally cleaner industrial wastewater treatment process for arsenic removal. Conversely, the efficiencies of arsenic removal using aluminum sulfate was not higher than 30% for wastewater samples and natural water sample spiked with As(III) as shown in Figure 4.23. For the mixture solution, the efficiency could be increased when the proportional As(V) in solution increases because aluminum ions can not precipitate As(III) and As(V) that was discussed earlier in the rulsult of full factorial design.

From these results, the efficiencies of arsenic removal are not different from the results from the calculation of model regression as shown in Table 4.13.

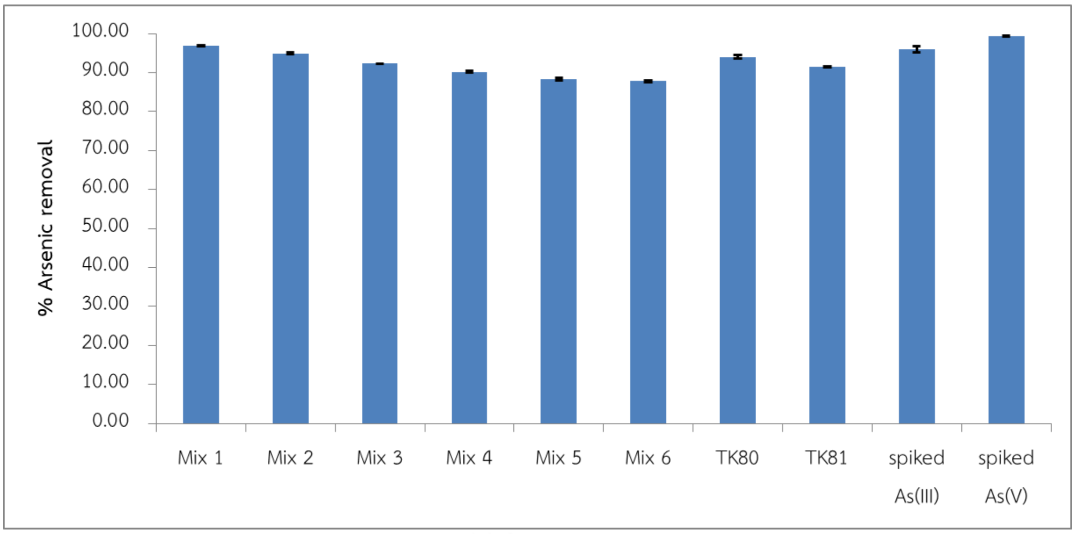


Figure 4.22 Efficiencies of arsenic removal for the mixtures (Mix1-6), the wastewater provided from petrochemical industry (TK80 and TK81) and natural water spiked with As(III) and As(V) concentrations of 90 mg L^{-1} determined by using the optimized conditions from RMS approach (pH 7 and 225 mg L^{-1} of ferric ions).

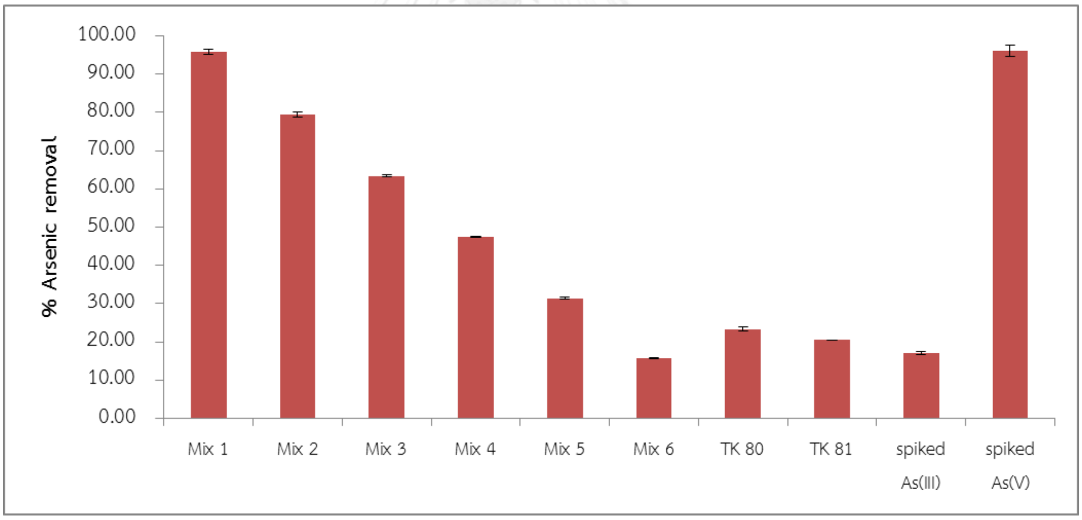


Figure 4.23 Efficiencies of arsenic removal for the mixtures (Mix1-6), the wastewater provided from petrochemical industry (TK80 and TK81) and natural water spiked with As(III) and As(V) concentrations of 90 mg L^{-1} determined by using the optimized conditions from RMS approach (pH 7 and 135 mg L^{-1} of Al ions).

Table 4.13 Actual and predicted values for arsenic removal of Mix1, Mix6, Spiked As(III) and spiked As(V)

	Ferric chloride		Aluminum sulfate	
	actual value	Predicted value	actual value	Predicted value
Spiked As(IIII)	96.05	92.52	17.12	15.34
Spiked As(V)	99.27	99.65	96.12	100.00
Mix1	87.77	92.52	15.75	15.34
Mix6	96.93	99.65	95.81	100.00

4.6 Jar test

The arsenic removal by coagulation in larger scale was investigated by Jar test method [39]. The results of Jar test for arsenic removal using ferric chloride and aluminum sulfate at optimized conditions are shown in Table 4.14. The efficiencies of arsenic removal are 96.13% and 21.66% using ferric chloride and aluminum sulfate, respectively. Therefore, ferric chloride is effectively suitable co-precipitant which can be used to remove arsenic in large scale for arsenic contaminated wastewater treatment.

Table 4.14 Result of jar test for the arsenic removal using ferric chloride and aluminum sulfate at optimized conditions.

Wastewater sample	Co-precipitant	% arsenic removal
TK81 (68.16 mg L^{-1} of As conc.)	Ferric chloride	96.13 ± 0.43
TK81 (68.16 mg L^{-1} of As conc.)	Aluminum sulfate	21.66 ± 0.35

CHAPTER V

CONCUSION

The co-precipitation for As(III) and As(V) using ferric chloride and aluminum sulfate as co-precipitant were evaluated using experimental design approach. The evaluating pH range for As(III) and As(V) in experimental design, types of co-precipitants and suitable settling time were studied by one factor at a time. The evaluated pH range was 5-10 for As(III) removal and 4-9 for As(V) removal. Ferric chloride is more effective than aluminum sulfate. The suitable settling time was 30 min for both As(III) and As(V) removal by co-precipitation. The full factorial design (FFD) and the central composite design (CCD) were used to evaluate the main and interactive parameters as pH solution, amount of co-precipitant and initial arsenic concentration. The maximum efficiencies with optimized conditions were determined using the Response Surface Methodology (RSM). The optimized conditions were determined in the CCD. The optimized condition for arsenic removal was pH solution of 7 and ferric ions concentration of 225 mg L^{-1} (corresponding to the mass ratio of Fe/As of 2.5 or the mole fraction of 3.34) while using aluminum sulfate was pH solution of 7 and aluminum ions concentration of 135 mg L^{-1} (corresponding to the mass ratio of Al/As of 1.5 or the mole fraction of 4.17).

These optimized conditions using ferric chloride were used to remove both As(III) and As(V) in mixture solutions, arsenic contaminated natural water including industrial wastewaters (TK80,TK81). The efficiencies were 93.98% and 98.48% for industrial wastewaters (TK80, TK81), 96.05% and 99.27% for natural water spiked with As(III) and As(V), respectively. While the efficiencies of arsenic removal using aluminum sulfate were 23.39% and 20.48% for industrial wastewaters (TK80, TK81), 17.12% and 96.12% for natural water spiked with As(III) and As(V), respectively.

For Jar test method, the efficiencies of removal of arsenic contaminated wastewater (TK81) were 96.13% and 21.66% using ferric chloride and aluminum sulfate, respectively. Therefore, ferric chloride is effective co-precipitant which can be used to remove arsenic in large scale for the treatment of arsenic containing wastewater in industries.

Suggestions for the future work

Coagulant aid and oxidation process should be studied to increase the efficiency of As(III) removal using aluminum sulfate or study more types of co-precipitant that can remove perfectly .both As(III) and As(V).

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APPENDIX

Table S1 The designed matrix and the responses of the nine extra experimental set of the CCD for As(III) removal with ferric chloride to use for the model validation. (X_1 = pH, X_2 = Ferric ions concentration, and X_3 = initial concentration of arsenic)

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
1	9.4 (1.3)	150 (0)	90 (0)	89.83
2	9.4 (1.3)	150 (0)	90 (0)	88.87
3	9.4 (1.3)	150 (0)	90 (0)	89.57
4	7 (-0.3)	225 (1)	90 (0)	96.05
5	7 (-0.3)	225 (1)	90 (0)	95.82
6	7 (-0.3)	225 (1)	90 (0)	95.98
7	7.7 (0.1)	225 (1)	45 (-1)	98.93
8	7.7 (0.1)	225 (1)	45 (-1)	99.02
9	7.7 (0.1)	225 (1)	45 (-1)	99.09
10	5.2 (-1.5)	150 (0)	90 (0)	82.63
11	5.2 (-1.5)	150 (0)	90 (0)	83.76
12	5.2 (-1.5)	150 (0)	90 (0)	83.79
13	7.7 (0.1)	225 (1)	135 (1)	90.89
14	7.7 (0.1)	225 (1)	135 (1)	90.79
15	7.7 (0.1)	225 (1)	135 (1)	90.69

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
16	7.7 (0.1)	75 (-1)	135 (1)	47.91
17	7.7 (0.1)	75 (-1)	135 (1)	47.43
18	7.7 (0.1)	75 (-1)	135 (1)	47.50
19	9 (1)	75 (-1)	90 (0)	53.54
20	9 (1)	75 (-1)	90 (0)	54.28
21	9 (1)	75 (-1)	90 (0)	54.80
22	6 (-1)	150 (0)	90 (0)	71.03
23	6 (-1)	150 (0)	90 (0)	72.02
24	6 (-1)	150 (0)	90 (0)	70.94
25	6 (-1)	225 (1)	90 (0)	83.54
26	6 (-1)	225 (1)	90 (0)	85.53
27	6 (-1)	225 (1)	90 (0)	83.68

Table S2 The designed matrix and the responses of the nine extra experimental set of the CCD for As(V) removal with ferric chloride to use for the model validation. (X_1 = pH, X_2 = Ferric ion concentration, and X_3 = initial concentration of arsenic)

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
1	7 (0.34)	225 (1)	90 (0)	98.30
2	7 (0.34)	225 (1)	90 (0)	98.51
3	7 (0.34)	225 (1)	90 (0)	98.12
4	5 (-1)	150 (0)	90 (0)	98.93
5	5 (-1)	150 (0)	90 (0)	99.07
6	5 (-1)	150 (0)	90 (0)	99.16
7	5 (-1)	75 (-1)	90 (0)	64.04
8	5 (-1)	75 (-1)	90 (0)	66.74
9	5 (-1)	75 (-1)	90 (0)	68.17
10	7.7 (0.81)	75 (-1)	45 (-1)	84.10
11	7.7 (0.81)	75 (-1)	45 (-1)	83.51
12	7.7 (0.81)	75 (-1)	45 (-1)	84.85
13	7.7 (0.81)	225 (1)	45 (-1)	98.86
14	7.7 (0.81)	225 (1)	45 (-1)	98.81
15	7.7 (0.81)	225 (1)	45 (-1)	99.02

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
16	5.2 (-0.87)	150 (0)	90 (0)	98.39
17	5.2 (-0.87)	150 (0)	90 (0)	98.82
18	5.2 (-0.87)	150 (0)	90 (0)	98.73
19	5.2 (-0.87)	150 (0)	14 (-1.7)	99.76
20	5.2 (-0.87)	150 (0)	14 (-1.7)	99.89
21	5.2 (-0.87)	150 (0)	14 (-1.7)	99.91
22	7.7 (0.81)	225 (1)	135 (1)	91.52
23	7.7 (0.81)	225 (1)	135 (1)	91.49
24	7.7 (0.81)	225 (1)	135 (1)	92.32
25	7.7 (0.81)	75 (-1)	135 (1)	33.26
26	7.7 (0.81)	75 (-1)	135 (1)	34.27
27	7.7 (0.81)	75 (-1)	135 (1)	32.42

Table S3 The designed matrix and the responses of the nine extra experimental set of the CCD for As(V) removal with aluminum sulfate to use for the model validation. (X_1 = pH, X_2 = Al ions concentration, and X_3 = initial concentration of arsenic)

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
1	7 (0.34)	135 (1)	90 (0)	99.66
2	7 (0.34)	135 (1)	90 (0)	99.43
3	7 (0.34)	135 (1)	90 (0)	99.82
4	5 (-1)	45 (-1)	90 (0)	78.63
5	5 (-1)	45 (-1)	90 (0)	76.42
6	5 (-1)	45 (-1)	90 (0)	80.09
7	5 (-1)	90 (0)	90 (0)	99.24
8	5 (-1)	90 (0)	90 (0)	99.24
9	5 (-1)	90 (0)	90 (0)	99.34
10	5 (-1)	135 (1)	90 (0)	99.78
11	5 (-1)	135 (1)	90 (0)	99.92
12	5 (-1)	135 (1)	90 (0)	99.92
13	7.7 (0.81)	45 (-1)	45 (-1)	84.81
14	7.7 (0.81)	45 (-1)	45 (-1)	87.96
15	7.7 (0.81)	45 (-1)	45 (-1)	87.92

Run	Actual value (coded value)			Response
	X_1	X_2	X_3	
16	7.7 (0.81)	135 (1)	45 (-1)	99.53
17	7.7 (0.81)	135 (1)	45 (-1)	99.70
18	7.7 (0.81)	135 (1)	45 (-1)	99.85
19	5.2 (-0.87)	90 (0)	14 (-1.68)	99.85
20	5.2 (-0.87)	90 (0)	14 (-1.68)	99.91
21	5.2 (-0.87)	90 (0)	14 (-1.68)	99.92
22	7.7 (0.81)	135 (1)	135 (1)	87.45
23	7.7 (0.81)	135 (1)	135 (1)	86.97
24	7.7 (0.81)	135 (1)	135 (1)	87.50
25	7.7 (0.81)	45 (-1)	135 (1)	45.36
26	7.7 (0.81)	45 (-1)	135 (1)	40.94
27	7.7 (0.81)	45 (-1)	135 (1)	40.88

VITA

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