REMOVAL OF ARSENIC FROM WASTEWATER USING MIXED METAL HYDROXIDES AND BIOPOLYMERS

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อาร์เซนิกเป็นหนึ่งในสารปนเปื้อนที่มีอยู่ในแหล่งน้ำเสีย ดังนั้นจึงมีหลากหลายวิธีที่มีถูกพัฒนาขึ้นมาเพื่อขจัดอาร์เซนิก โดยที่สำหรับในการศึกษานี้จะเป็นการศึกษาถึงประสิทธิภาพในการขจัดอาร์เซนิกโดยวิธีการตกตะกอนร่วมด้วยการผสมผสานของเกลือของโลหะที่เป็นที่รู้จักกันอย่างแพร่หลายในแง่ของการนำมาขจัดอาร์เซนิก เช่น เฟอร์ริกคลอไรด์ หรืออลูมิเนียมคลอไรด์กับเกลือของโลหะที่มีความเป็นมิตรต่อสิ่งแวดล้อม เช่น แมกนีเซียมคลอไรด์ หรือแคลเซียมคลอไรด์ โดยที่จะเรียกการผสมผสานกันของเกลือของโลหะเหล่านี้ว่า “ระบบโลหะผสม” และช่วยลดความเป็นพิษของตะกอนที่เกิดขึ้นภายหลังจากการตกตะกอนร่วม โดยการใช้โลหะผสมเป็นสารช่วยสร้างตะกอน และใช้พอลิเมอร์ชีวภาพชนิดแอลจิเนต หรือไคโทซานเป็นสารช่วยรวมตะกอนเพื่อช่วยเพิ่มประสิทธิภาพในการขจัดอาร์เซนิก โดยภายใต้ภาวะที่เหมาะสมที่สุดในการตกตะกอนร่วมเพื่อขจัดอาร์เซนิกจากน้ำเสียสังเคราะห์นั้นจะทำให้ได้ค่าร้อยละในการขจัดอาร์เซนิกเท่ากับ 95.4 และ96.8 ที่ค่าความเป็นกรดเบสเท่ากับ 9 โดยการใช้อัตราส่วนระหว่างโลหะผสมของแมกนีเซียมกับเหล็กต่ออาร์เซนิก และแคลเซียมกับเหล็กต่ออาร์เซนิกเท่ากับ 2.5 ในการตกตะกอนร่วมตามลำดับ และยิ่งไปกว่านั้นสำหรับระบบที่ใช้การผสมผสานกันระหว่างโลหะผสมกับพอลิเมอร์ชีวภาพยังสามารถทำให้ประสิทธิภาพในการขจัดอาร์เซนิกมีค่าเพิ่มขึ้นที่ค่าความเป็นกรดเบสเท่ากับ 9 โดยการใช้แอลจิเนตเข้มข้นร้อยละ 0.7 โดยน้ำหนักต่อปริมาตรร่วมกับระบบโลหะผสมที่มีอัตราส่วนของแมกนีเซียมกับเหล็กต่ออาร์เซนิกเท่ากับ 1.25 และสามารถช่วยเพิ่มประสิทธิภาพในการขจัดอาร์เซนิกที่ค่าความเป็นกรดเบสเท่ากับ 7 สำหรับการใช้ร้อยละ 0.7 โดยน้ำหนักต่อปริมาตรของแอลจิเนตร่วมกับระบบโลหะผสมที่มีอัตราส่วนของแคลเซียมกับเหล็กต่ออาร์เซนิกเท่ากับ 1.25, 1.5 และ2.0 อีกด้วย

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ลายมือชื่อนิสิต ....
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Arsenic is one of the contaminants in wastewater which becomes a worldwide environmental problem. Therefore, several simple and cost-effective techniques have been developed for arsenic removal. This study reports on the removal of arsenic by coprecipitation method with variable combinations of the well-known metal salts, such as $FeCl_3$ or $AlCl_3$ with the environmentally friendly inorganic metal salts, such as $MgCl_2$ or $CaCl_2$, which is called “mixed metal system”. Moreover, for improving the low toxicity from sludge production, hence the coprecipitation techniques using mixed metal salts as coagulants combine with biopolymers (alginate or chitosan) as flocculants for arsenic removal were also studied. Under the optimum conditions, the results showed that the arsenic removal efficiency from simulated wastewater were about 95.4% and 96.8%, at pH9 by using 2.5MgFe/As and 2.5CaFe/As, consecutively. In addition, the arsenic removal efficiency of the combination between mixed metal and biopolymer systems were increased at pH9 for 0.7%w/v of alginate combine with 1.25MgFe/As, and it also increased at pH7 for 0.7%w/v of alginate combine with 1.25, 1.5 and 2.0CaFe/As system.

Field of Study:	Chemistry	Student's Signature ....
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CHAPTER I

INTRODUCTION

1.1 Statement of problem

Nowadays, growing technologies and industries bring about one of the major environmental problems, which is the contamination of heavy metals in water. Arsenic is a well-known toxic element, which can contaminate into aquatic environment by natural weathering reactions and anthropogenic activities such as the combustion of fossil fuels, petroleum refining processes and the use of arsenic pesticides, herbicides in agriculture which create additional impact to the environment. Arsenic compounds which can exposure to the living organisms by drinking water, have been recognized as group 1 carcinogens by International Agency for Research on Cancer (IARC). Moreover, long-term drinking water exposure to arsenic can cause cancer, skin damage, cardiovascular diseases, and neurological disorders for both humans and animals. Therefore, the World Health Organization (WHO) and the Pollution Control Department (PCD) limits the value of 10 ppb (0.01 mg/L) and 250 ppb (0.25 mg/L) for arsenic in drinking water and wastewater standard, respectively [1, 2]

Arsenic can be presented in the environment in several forms including -5, -3, 0, +3 and +5 of oxidation states, but the only two forms occur mainly in water: arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}), which refer to As(III) and As(V), respectively . Arsenite remains as neutral species (H_3AsO_3) below a pH of 9.2 while arsenate exists as negative species ($H_2AsO_4^-$,$HAsO_4^{2-}$) in a pH range of 2-12 [3]. Furthermore, the previous research showed that arsenite is more difficult to be removed from water and lethal around 60 times than arsenate [4].

Since arsenic pollution has become one of the major environmental problems; thus, several conventional techniques have been developed for arsenic removal from contaminated wastewater including oxidation-precipitation, coagulation-flocculation, adsorption, ion- exchange, and membrane filtration techniques. Some of these techniques require an oxidation step as pre-treatment to convert arsenite (As(III)) to arsenate (As(V)) for improving the arsenic removal efficiency in a wide range of optimal conditions such as pH of the solution [4]. Coprecipitation or coagulation-flocculation is one of the most popular techniques which can reduce the arsenic in wastewater due to the fact that its simplicity, effectiveness, and unnecessary pre-treatment step.

Among coprecipitation technique, the use of well-known inorganic metal salts such as ferric chloride or aluminum sulfate (Alum), as coagulants to precipitate arsenic has been one of the most popular chemicals due to their inexpensive yet effective and ready availability. However, the use of inorganic metal salts system or chemical methods have some disadvantages, for example, it can produce a large amount of sludge which can cause the potential toxicity to human health, or other living organisms [5]. Alternatively, the use of biopolymers as flocculants or coagulant aids also has useful properties over inorganic metal salts such as large flocs formation and high settling properties [6].

For improving the arsenic removal, cost-efficiency, biodegradability and low toxicity from sludge production, hence the coprecipitation techniques which use mixed metal hydroxide as coagulants, or the use of mixed metal salts as coagulants combined with biopolymers as flocculants have been studied [7]. Arsenic is easily coprecipitated with coagulants (inorganic metal salts), then the flocculants (biopolymers) is added to form the larger particles or allowed to settle down by themselves. Moreover, the use of mixed metal salts as coagulants (binary system) or the use of mixed metal salts combined with biopolymers as flocculants (ternary system) probably reduces the dosage of coagulants needed which using only one type of metal salt (single system). Based on biopolymers which act as polymeric flocculants or coagulant aids, chitosan and alginate are interesting because of their unique properties.

1.2 Objectives

The objectives of this research include (1) To study the compositions and the optimum conditions of mixed metal salts for arsenic removal using coprecipitation method and (2) To study the optimum conditions of biopolymers for increasing the performance of arsenic removal.

1.3 Scope of research

The scope of this research firstly involved the coprecipitation of arsenic with mixed metal salt (M^{2+}/M^{3+}) systems including magnesium chloride/ ferric chloride (Mg/Fe), calcium chloride/ ferric chloride (Ca/Fe), magnesium chloride/ aluminum chloride (Mg/Al) and calcium chloride/ aluminum chloride (Ca/Al). Then, factors affecting the arsenic removal by using mixed metal salts including the pH of the solution, mole ratio between divalent metal (M^{2+}) and trivalent metal (M^{3+}), mole ratio between mixed metal and arsenic ($M^{2+}M^{3+}/As$), step of pH adjustment, and retention time were evaluated to find out the optimum conditions for arsenic removal process by coprecipitation method. Furthermore, the coprecipitation techniques which use mixed metal salts as coagulants combined with biopolymers (alginate or chitosan) as flocculants for improving the arsenic removal efficiency and reducing the dosage of coagulants (metal salts) needed, were also studied. Then, the effects of biopolymer types, biopolymer concentration, retention time and pH were also evaluated. Finally, the effective system with the optimum condition for arsenic removal was validated in the real industrial wastewater sample from a petrochemical company in Thailand.

1.4 Benefits

The coprecipitation technique by using mixed metal salts as coagulants, or the use of mixed metal salts, as coagulants combined with biopolymers as flocculants systems which being effective for arsenic removal was obtained.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Chemistry of arsenic

Arsenic is a metalloid element in the periodic table, which naturally occurs in the environment. It is a well-known of poison that is proven to have negative influence on environmental and living organism health including human and animal. Most environmental problems of arsenic are the result of mobilization under natural conditions including natural weathering reactions, biological activities, geochemical reactions, volcanic emissions and other anthropogenic activities. However, combustion of fossil fuels, mining activities, petroleum refining, using of arsenic pesticides and herbicides, and using of arsenic additives in livestock feed also increase arsenic concentration and create additional impacts to the environment.

Arsenic is an element which can be found in environment in different oxidation states such as +5, +3, 0, -3 and -5 depending on redox potential and pH conditions. Additionally, arsenic occurs in the environment mainly as inorganic arsenic oxides such as arsenite (As(III)), and arsenate (As(V)) [7]. In general, arsenite with oxidation state +3, is predominant species under reducing conditions and it exists as neutral species or non-ionized form (H_3AsO_3) at pH which less than 9.2, and it is changed to its ionized forms like $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} only in strong basic conditions (pH>9.2). While arsenate with oxidation state +5, become dominating species under oxidizing conditions and it can be found in ionized forms at pH range 2-14, resulting in the fact that negative species like $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} exist [8].

The deprotonations of arsenite (As(III)) and arsenate (As(V)) under different pHs are summarized in Figure 1 from the pK_a values [8].

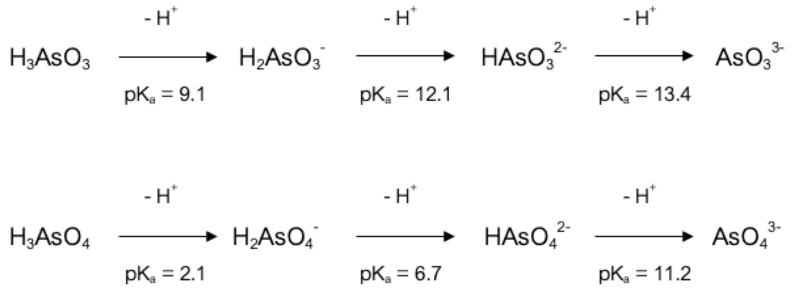

Figure 1. Dissociation of Arsenic species (As(III) and As(V))

The distribution of arsenite (As(III)) and arsenate (As(V)) species under different pH conditions are shown in Figure 2, consecutively [9].

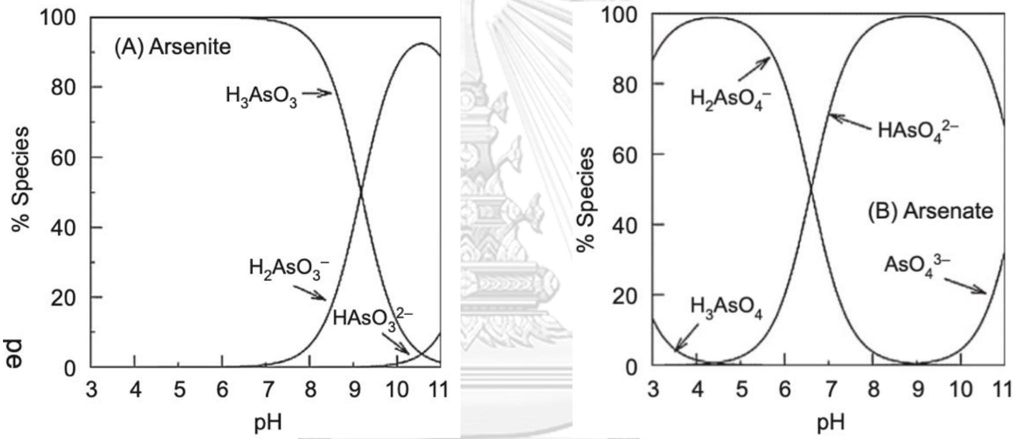

Figure 2. Distribution of Arsenite (As(III)) and Arsenate (As(V))

Moreover, the organic form of arsenic can also be found in natural water such as monomethyl arsenious acid (MMA (III)), monomethyl arsenic acid (MMA (V)), dimethyl arsenious acid (DMA (III)), and dimethyl arsenic acid (DMA (V)). But these several organic forms of arsenic are not the major significance in drinking water treatment process because of their concentrations are lower than 1 ppb (1 μg/L) [9].

2.1.2 Arsenic toxicity

Arsenic is a widely well-known toxic element. The arsenic in a high dose was used as a poison, even in the small concentration with dosing for a long period can also cause chronic diseases [10]. The toxicity of arsenic can differ greatly due to the effect of inorganic or organic forms, solubility, valence and physical states. Generally, arsenite (As(III)) is more lethal around 60 times than arsenate (As(V)), and it also more difficult to be removed from wastewater due to its neutral form in a wide range of pH. Moreover, the effect of arsenic can be distinguished between a short- and long- term exposure. For short-term with high dose exposure of arsenic, it can affect an ingestion and it results in a violent vomiting and other gastrointestinal symptoms, which can occur after 30-60 minutes, then the multiorgan failures may occur and followed by death [11].

Once arsenic released, their species can undergo in different processes, resulting in the distribution of arsenic into the environment by the general pathways which involving the living organisms (biota), as shown in Figure 3.

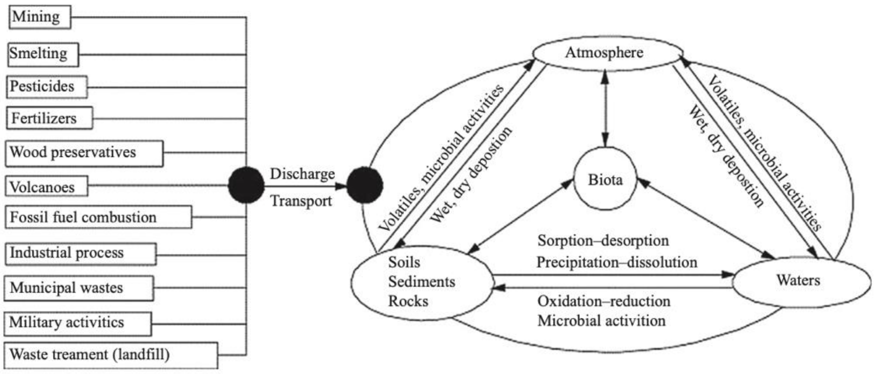

Figure 3. Simplified diagram of Arsenic cycle

In general, a high probability region of arsenic contamination which appears across the world is in groundwater. Therefore, the arsenic which releasing to the environment can be widespread in other drinking resource, and its can be presented in food, especially in fish which live in contaminated wastewater [12].

Moreover, the symptoms of toxicity from arsenic species on human organ systems are listed in Table 2.1 [13].

Table 2.1 Toxicity of arsenic on human organ systems

Organ Systems	Symptoms or signs
Gastrointestinal	Abdominal pain, Diarrhea, Vomiting
Hepatic	Fatty infiltration, Central necrosis
Cardiovascular	Cardiac abnormality, Congestion heart failure, Hypotension
Neurological	Behavior, Confusion, Memory loss
Respiratory	Irritation of nasal mucosa
Genitourinary	Bladder, Kidney, Ureter and all Urethral cancer risk

Additionally, the lethal dose (LD_{50}), which is the amount of a toxic agent that is sufficient to kill 50 percent of animal population in a certain time, of some arsenic compound is shown in Table 2.2 [13, 14].

Table 2.2 Lethal dose (LD_{50}) of some arsenic compound

Arsenic compounds		LD_{50} (mg arsenic/kg body weight)
Ingestion	- Arsenic trioxide	15-293
	- Sodium arsenite	6-24
	- Sodium arsenate	6
	- Calcium arsenate	53
	- Lead arsenate	231
Dermal absorption	- Calcium arsenate	> 400
	- Lead arsenate	> 500
Intramuscular absorption	- Sodium arsenite	21
	- Sodium arsenate	8

Since arsenic pollution has become one of the major environmental problems; thus, the effective arsenic removal techniques have been studied. The various techniques for arsenic removal from contaminated wastewater such as oxidation-precipitation, coagulation-coprecipitation, ion-exchange, adsorption, and membrane filtration are provided and described more detail in the next section.

2.2 Methods for arsenic removal

Currently, there are many technologies available for the removal of arsenic from contaminated wastewater including oxidation-precipitation, coagulation-coprecipitation, ion-exchange, membrane filtration and adsorption techniques. However, the decision about the selection of the treatment shall be based on water chemistry and process characteristics. Additionally, the general trend in water treatment process is to use as less chemicals and energy as possible, for reducing cost and energy consumption. For better understanding about a detail of arsenic removal technologies based on sorption of arsenic as a rapid and inexpensive is roughly described in the following subsections [15-17].

2.2.1 Oxidation method

Arsenic is normally present in groundwater in arsenite (As(III)) and arsenate (As(V)) forms in different proportions. It is well known that arsenite is more difficult to be removed from water than arsenate. Therefore, the oxidation step as a pretreatment to convert arsenite to arsenate is the way for improving the efficiency of arsenic removal process. However, oxidation step is only a pretreatment step which must be combined with other techniques such as precipitation or adsorption. Additionally, arsenite can be oxidized by various chemical oxidizing agents including ozone (O_3), hypochlorous (HClO) and potassium permanganate (MnO_4) etc. Hence, some of the oxidation reactions by general oxidizing agents, are summarized and presented in Table 2.3 [18].

Table 2.3 Chemical oxidants and their reactions with arsenite (As(III))

Oxidants	Reactions
Chlorine (Cl_2)	$H_3AsO_3 + HOCl \rightarrow AsO_4^{3-} + Cl^- + 4H^+$
Chlorine dioxide (ClO_2)	$H_3AsO_3 + 2ClO_2 + H_2O \rightarrow AsO_4^{3-} + 2ClO^{2-} + 5H^+$
Chloramine (NH_2Cl)	$H_3AsO_3 + NH_2Cl + H_2O \rightarrow AsO_4^{3-} + NH_4^+ + Cl^- + 3H^+$
Hydrogen peroxide (H_2O_2)	$H_3AsO_3 + H_2O_2 \rightarrow AsO_4^{3-} + H_2O + 3H^+$
Ozone (O_3)	$H_3AsO_3 + O_3 \rightarrow AsO_4^{3-} + O_2 + 3H^+$
Permanganate (MnO_4^-)	$3H_3AsO_3 + 2MnO_4^- \rightarrow 3AsO_4^{3-} + 2MnO_2 + 7H^+ + H_2O$
Ferrate (FeO_4^{2-})	$3H_3AsO_3 + 2FeO_4^{2-} + H_2O \rightarrow 3AsO_4^{3-} + 2Fe(OH)_3 + 5H^+$

Moreover, there are the other types of oxidation process which have been used as pre-treatment step such as biological oxidation, air oxidation, and solar oxidation etc. Aside from many chemicals oxidizing agents, atmospheric oxygen (O_2), as well as bacteria or microorganisms, which have already been used to oxidize arsenite to arsenate in water. The performance and their operating conditions of some oxidizing agent to convert arsenite to arsenate, are enumerated in Table 2.4 [19].

Table 2.4 Different oxidants with their operating conditions and efficiencies

Oxidants	pH	Initial Conc.	Type of water	Remarks
Oxygen (O_2)	7.6-8.5	46-62 µg/L	Groundwater	- 5 days were needed to oxidize 57% and 54% using pure O_2 and air, respectively.
Chlorine (Cl_2)	8.3	300 µg/L	Deionized water	- Completely oxidized when its initial conc. was greater than 300 µg/L. (0.99 mg Cl_2, mg As)

Chlorine dioxide (ClO_2)	8.1	50 µg/L	Groundwater	- After 1 hour, 86% oxidation yield was achieved.
Monochloroamine (NH_2Cl)	8.1	50 µg/L	Groundwater	- After 18 hours, 60% oxidation yield was achieved.
Hypochlorite (ClO^-)	7.0	500 µg/L	Groundwater	- Completely oxidized when giving a hypochlorite conc. of 500 µg/L.
Hydrogen peroxide (H_2O_2)	7.5-10.3	50 µg/L	Freshwater and seawater	- Oxidation yield was improved when pH was increased (7-10).
Potassium permanganate ($KMnO_4$)	8.1	50 µg/L	Groundwater	- After 1 minute, oxidation was completed.
Photocatalytic oxidation (UV/ H_2O_2)	8.0	100 µg/L	Groundwater	- 85% oxidation yield was achieved, at UV dose of 2000 mJ/cm^2.

Atmospheric oxygen (O_2) is one of the most oxidative agents which are commonly and easily used by contact the solution with atmospheric air. Nevertheless, oxidation process of As(III) with oxygen as an oxidizing agent is a very slow process, which can take days or weeks to complete. On the other hand, the oxidation process with chemicals such as chlorine (Cl_2)

or potassium permanganate ($KMnO_4$), can be more rapidly oxidize As(III) to As(V) than oxygen, as presented in Table 2.4.

Thus, the oxidation efficiency of arsenic by oxidation process, oxidants should be considered and selected carefully. However, the major drawbacks of the oxidation step which used chemical agents as oxidants, is the production of harmful disinfection by-products (DBPs) [19].

2.2.2 Coprecipitation method

Coprecipitation method is a method which has been widely used for arsenic removal, because of it can remove not only arsenic, but it can also remove many suspended and dissolved matters from water. This method based mostly on aluminum and iron compounds such as aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride ($FeCl_3$), which are effective for removing arsenic from contaminated wastewater. First, aluminum or ferric hydroxide micro-flocs are formed rapidly. Then, the agglomeration of micro-flocs into larger easily settable flocs is occurred, consecutively. Additionally, during this coprecipitation or coagulation-flocculation process, all kind of micro-particles and negatively charged ions like arsenite or arsenate are attached to the flocs by electrostatic interaction, resulting in the removal of arsenic or other negatively charged suspended colloids [20].

Coprecipitation process occurs as a result of a combination of different mechanisms including adsorption or precipitation, depend on the conditions of the solutions (pH, ionic strength, ion concentration, and the present of co-existing ions), as well as the surface conditions (crystal states or the form of minerals). Furthermore, arsenic can be also adsorbed onto the coagulated flocs such as solid hydroxide surface site, or coprecipitated with other precipitating species [20].

The possible chemical equations of metal coprecipitation are shown as follows:

Metal dissolution

$$M \cdot H_2O \longrightarrow M^+ + A^- + H_2O \tag{2.1}$$

Metal precipitation

$$M^+ + H_2O \longrightarrow M(OH)_n + H^+ \tag{2.2}$$

Coprecipitation

$$H_2AsO_4^- + M(OH)_n \longrightarrow M\text{-}As\ (complex) + Other\ products \qquad (2.3)$$

Where M is a metal ion.

However, the filtration or separation step is required to ensure a complete removal of all particles after the coprecipitation step was done.

Moreover, the performance compared of some chemical coagulant for arsenic removal will be shown in Table 2.5 [19, 20].

Table 2.5 Different coagulants with their efficiencies for arsenic removal

Coagulants	Initial Conc.	Remarks
Ferric Chloride ($FeCl_3$)	2 mg/L	- Optimum $FeCl_3$ dosage was 30 mg/L. - As(III) and As(V) removal efficiencies were 45% and 75%, respectively.
Ferric Sulfate ($Fe_2(SO_4)_3$)	1 mg/L	- Optimum $Fe_2(SO_4)_3$ dosage was 25 mg/L - As(III) removal efficiency was about 80%.
Alum ($Al_2(SO_4)_3$)	20 µg/L	- Optimum Alum dosage was 40 mg/L. - As(V) removal efficiency was about 90%.
Zirconium (IV) Chloride ($ZrCl_4$)	50 µg/L	- Optimum $ZrCl_4$ dosage was 2 mg/L - As(III) and As(V) removal efficiencies were 8% and 55%, respectively.
Zirconium (IV) Oxychloride ($ZrOCl_2$)	50 µg/L	- Optimum $ZrOCl_2$ dosage was 2 mg/L - As(III) and As(V) removal efficiencies were 8% and 59%, respectively.

Titanium (III) Chloride ($TiCl_3$)	50 µg/L	- Optimum $TiCl_3$ dosage was 2 mg/L. - As(III) and As(V) removal efficiencies were 32% and 75%, respectively.
Titanium (IV) Chloride ($TiCl_4$)	50 µg/L	- Optimum $TiCl_4$ dosage was 2 mg/L. - As(III) and As(V) removal efficiencies were 26% and 55%, respectively.
Titanium (IV) Oxychloride ($TiOCl_2$)	50 µg/L	- Optimum $TiOCl_2$ dosage was 2 mg/L. - As(III) and As(V) removal efficiencies were 20% and 37%, respectively.
Titanium (IV) Sulfate ($Ti(SO_4)_2$)	1 mg/L	- Optimum $Ti(SO_4)_2$ dosage was 25 mg/L. - As(III) removal efficiency was about 90%.

Generally, the increasing of chemical coagulants dosages, the higher arsenic removal efficiency can be achieved. Therefore, the major drawback of coprecipitation or coagulation-flocculation process is the high amounts of arsenic-concentrated sludge production.

2.2.3 Ion exchange method

Ion exchange is one of the methods for arsenic removal in which ions are exchanged between the solid resin phase and solution phase. The solid resin is typically an elastic three-dimensional hydrocarbon network which containing a large number of ionizable groups electrostatically bound to the resin [20]. In addition, ion exchange resins can be divided into four types depend on their types of ion that exchanged, and acid or base property including.

- Strongly acidic (cation exchange): Sulfonate ($-SO_3^-$)
- Weakly acidic (cation exchange): Carboxylate ($-COO^-$)
- Strongly basic (anion exchange): Quaternary amine ($-N^+(CH_3)_4$)
- Weakly basic (anion exchange): Tertiary amine ($-N(CH_3)_3$)

Arsenate (As(V)) can be removed from water by using anion exchange resin while arsenite (As(III)) is not removed by this resin because of it neutral forms or uncharged species at a pH of less than 9.2. Therefore, the oxidation step of arsenite to arsenate as a pretreatment step was required for improving the arsenic removal efficiency for ion exchange process. However, the excess of oxidizing agent needs to be completely removed before the ion exchange step in order to avoid the damage of sensitive resins. Additionally, as the resin becomes exhausted, it needs to be regenerated with salt solution (sodium chloride (NaCl)) [20].

The arsenic exchange and regeneration equations with common salt solution as regeneration agent are shown as follows:

Arsenic exchange

$$2R\text{-}Cl + HAsO_4^{2-} \longrightarrow R_2HAsO_4 + 2Cl^- \quad (2.4)$$

Regeneration

$$R_2HAsO_4 + 2Na^+ + 2Cl^- \longrightarrow 2R\text{-}Cl + HAsO_4^{2-} + 2Na^+ \quad (2.5)$$

Where R stands for ion exchange resin.

Furthermore, the arsenic removal capacity of ion exchange process, is dependent on sulfate and nitrate contents of raw water, because sulfate and nitrate are exchanged before arsenic. Hence, ion exchange process for an effective arsenic removal is only applicable for low- sulfate and nitrate source water.

For the disadvantages of ion exchange process, they are not only the strongly pH dependence and it applicable for some source of water, but it is also about the releasing of noxious chemical reagents which used in the resin regeneration into the environment.

2.2.4 Membrane filtration method

Membrane filtration method is one of the methods which can remove the contaminants in water such as bacteria, salts, and heavy metals. For the membrane filtration process, the water is allowed to pass through special filter media which physically retain the impurities present in water. The movement of the molecules across the membrane needs a driving force like the difference pressure between the two sides of membrane. Moreover, the membrane filtration method can be categorized into four categories by the pore size of the membrane: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (OR). All of these membranes are effective to remove arsenic, especially NF and RO which represent an excellent arsenic removal efficiency. However, this process is usually expensive than other arsenic treatment methods. Therefore, it is not commonly used for arsenic removal from wastewater, but it is suitable for preventing the micro-organisms passing through the membrane to diminish the harmful diseases [19, 20]. In addition, the characteristics of these four membrane processes (MF, UF, NF, OR) are summarized in Table 2.6.

Table 2.6 Overview of pressure-driven membrane processes and their characteristics

Parameters	Microfiltration	Ultrafiltration	Nanofiltration	Reverse Osmosis
Pore size	100-10,000 nm	2-100 nm	3-20 nm	5-120 nm
Monovalent ions	-	-	-	+
Multivalent ions	-	-	- / +	+
Small organic compounds	-	-	- / +	+
Macromolecules	-	+	+	+
Particles	+	+	+	+
Applications	Clarification, Pretreatment, Sterilization	Removal of macromolecule, bacteria, virus	Removal of organic compounds	Removal of salts

2.2.5 Adsorption method

Adsorption is a widely used method for arsenic removal because of its high removal efficiency, easy operation, low cost and sludge free. Adsorption is a process that uses solids (adsorbent) for removing substances (adsorbate) from either gaseous or liquid solutions phase to the surface of solid phase adsorbent. During the adsorption process, the contaminants are adsorbed on adsorbent surfaces. Nevertheless, when the adsorption sites become filled, which means that the efficiency for removing the desired impurities becomes zero, then the contaminated adsorbent might be regenerated. Moreover, the saturated and exhausted sorbent need to be replacement after four or five regenerations [19, 20].

In addition, the efficiency of adsorption process depends on the physical and chemical properties of adsorbate and adsorbent with the conditions that used in the adsorption process such as pH of solution, contact time, and initial concentration of adsorbate. Depending upon the nature of the interaction between adsorbate and adsorbent involved, two main types of adsorption process, including physical adsorption (physisorption) and chemical adsorption (chemisorption) may be distinguished in the next following subsections.

2.2.5.1 Type of adsorption

i) Physical adsorption (Physisorption)

Physisorption or physical adsorption is the interaction between adsorbate and adsorbent in which an adsorbate attracts to the surface of adsorbent via Van-der Waal’s or electrostatic forces which are weak forces. Moreover, physisorption occurs quickly and may be leading to the formation of multilayer of adsorbate on adsorbent surfaces. Therefore, the maximum adsorption capacity of this process depends on the pore volume and surface area of adsorbent [21].

ii) Chemical adsorption (Chemisorption)

In contrast to physisorption, chemisorption or chemical adsorption involves the formation of chemical bonds such as covalent bond between adsorbates and functional groups on the surface of adsorbent. Therefore, the interaction as chemisorption is strongerthan physisorption process. Moreover, chemisorption occurs only as monolayer, and may be followed by the formation of multilayer which are bound by physical forces [21].

2.2.5.2 Type of adsorbent

Adsorbents are very important in the adsorption process due to the fact that it affects to the removal efficiency of the adsorption process. Moreover, adsorbents must be inexpensive and good capacity for analyte adsorption which refers to high number of active sites on their adsorbent surface [22].

Adsorption technique has attracted much attention because of the several advantages such as, it does not use large amount and additional chemicals, it is easy to set up in removal process, and it also does not produce harmful by-products. Moreover, nowadays several materials have been used in their natural forms for adsorption process, without further treatment was required. Thus, adsorption process becomes one of the techniques of cost effectiveness. But on the other side of adsorption process, as the adsorbents get more saturated or exhausted, then the regeneration or the replacement of sorbents after four or five regeneration was needed.

Furthermore, all of the methods with their advantages or disadvantages for arsenic removal, which are mentioned above are concluded in Table 2.8 [15-22].

Table 2.7 Summarization of common arsenic removal methods

Methods	Chemicals/ Types	Advantages	Disadvantages
Oxidation	Air (O_2)	- Simple operation - Low cost	- Slow process
	Chemicals (Cl_2,ClO_2,$KMnO_4$,)	- Rapid process	- Produce disinfection by- products (DBPs)
Coprecipitation	Alum ($Al_2(SO_4)_3$)	- Simple operation - Low cost - Available chemicals	- Produce toxic sludge - Pre-oxidation may be needed
	Iron ($FeCl_3$)	- Simple operation - Common chemical - Effective than alum	- Produce toxic sludge - Medium removal of As(III)
Ion exchange	Cation- and anion- exchange resins	- Less dependent on pH of water - Ion-specific resin	- High cost - High-tech operation - Life of resins
Membrane filtration	MF, UF, NF and RO	- High removal efficiency	- Very high cost - High-tech operation
Adsorption	Activated carbon or alumina	- Well known and commercially available	- Replacement needed after four or five regeneration

Among the available technologies, arsenic removal by coprecipitation technique is one of the techniques, which is effective for arsenic removal by using low cost and also available chemicals such as ferric compounds or aluminum compounds. Therefore, coprecipitation method is one of the common choices for industrial to remove the arsenic from wastewater due to their simple, inexpensive yet effective process. However, the use of inorganic salts as coagulants in coagulation process may also have negative effect on both of human and environment. Hence, nowadays a number of compounds such as natural- or bio- polymers, or other polyelectrolytes, are being used as flocculants to combine with traditional metal salts in flocculation process, for improving the removal efficiency or being used to replace the metal salts for reducing the toxic sludge production from chemicals using [23].

2.3 Coagulation and Flocculation

Coagulation and flocculation are well-known techniques owing to its simplicity and effectiveness, for wastewater treatment from the environmentally unfriendly industrial processes. They are typically used for treatment of wastewater which containing colloids (suspended particles) or metal ions. Moreover, coagulation and flocculation are often used in combination as shown in Figure 4, for improving the removal efficiency and achieving the most cost effective of wastewater treatment process based on various coagulants and flocculants, respectively [24].

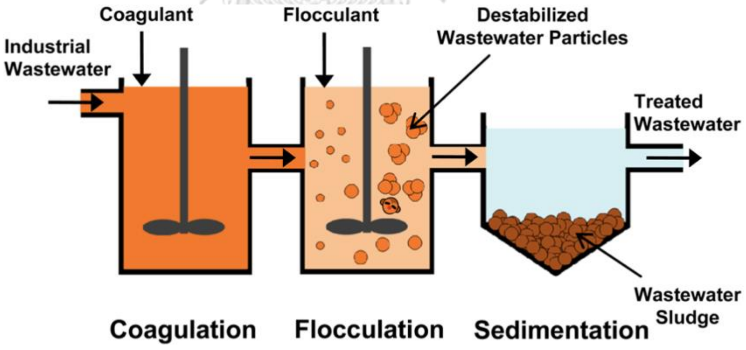

Figure 4. Coagulation-Flocculation-Sedimentation process

For the coagulation process, the small-suspended colloids in water are destabilized by addition of coagulants with an opposite charge of the suspended solids. Once the charge of the suspended solids is destabilized, the destabilized particles are capable of sticking together or aggregation, and settle down, consecutively. Furthermore, for improving the settle down of small particles efficiency or increasing the particles size from micro-flocs to visible suspended particles, organic- or inorganic- polymeric flocculants with flexible long chain conformation are sometimes added after coagulation process as coagulant aids. These polymeric flocculants may be added to help the adsorption or connection of various colloidal particles in water to form large flocs or macro-flocs, which can be ready and effectively removed by sedimentation process [25].

Generally, coagulation and flocculation efficiency depend largely on the selection of coagulants and flocculants. Different coagulants and flocculants exhibit different coagulation and flocculation performance due to their different structural characteristics, charge characteristics, ionic properties, special functional groups, and molecular weight. Due to the different characteristics of various types of target pollutants, a suitable coagulant and flocculant should be selected according to the coagulation and flocculation mechanisms.

However, the possibility of disease while using the conventional metal coagulants such as ferric or aluminum metal salts, has become one of the issues for wastewater treatment via coagulation-flocculation process. Therefore, the special attention has shift towards by using natural- or bio- polymer which are more environmentally friendly because of their biodegradability property [26].

2.3.1 Colloids and their stability

The fundamental states of matter are solids, liquids, and gases. If one of these states is finely dispersed in another, it will be “colloidal system” such as aerosols, emulsions, and colloidal suspensions etc. In most case of colloidal particles, each particle carries a like charge and nearly colloidal impurities in water which are negative charge in an aqueous environment. Consequently, the negative charge on the colloidal surface which is called “zeta potential” can create repulsive force between the charge that keep the particles apart and prevent their agglomeration. Moreover, the stability of suspension of colloid system depends on pH, temperature, and ionic strength of the solvent, which affect to the surface properties of colloids. For more understanding about colloidal stability and zeta potential, double layer theory was also explained in the next following subsection [26].

2.3.1.1 Double layer theory

In a solution, the liquid layer (double layer) surrounding the particle exists as two parts: inner region (stern layer) is the primary charge of the colloids attracts ions of the opposite charge, where the ions are strongly bound by the electrostatic and van der Waals forces, and the outer region (diffuse layer) is the co-ions of primary charge in the stern layer, where they are less firmly associated ions. As shown in Figure 5, it is not only the representation of liquid layer which is called “double layer” surrounding the particles, but it also represents the zeta potential, which is the potential at surface of colloids [26].

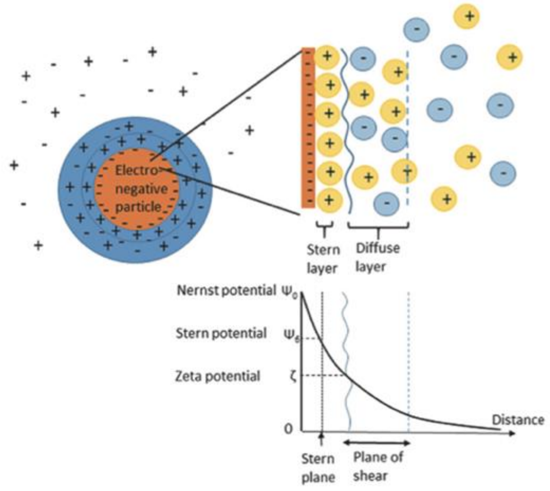

Figure 5. Electric double layer around a negative charged colloid

Furthermore, the indication of potential stability of colloidal system is the magnitude of the zeta potential. Providing the suspension particles which have a large negative or positive charge on the surface of colloid (zeta potential), the particles will tend to repel each other by electrostatic repulsion which resulting in the dispersion of particles in the suspension solution. For the colloids in water, the particles with zeta potentials more positive than +30 or more negative than -30 mV, are usually acquired due to the presence of its charged surface, which is called “electrostatic or charge stabilization” [26, 27].

However, coagulation and flocculation are defined as the destabilization processes which normally used chemical coagulants to neutralize the surface charges of those suspension colloids or particles, then induce them to make contact for the formation of larger particles, and giving them rise to agglomeration by flocculants, respectively. Moreover, the commonly used inorganic metal salts as coagulants can be divided into two parts: based on aluminum and iron, to obtain high charge neutralization effects on the basis of DLVO (Derjaguin, Landau, Verwery, and Overbeek) theory, which were described in the following subsection [26, 27].

2.3.1.2. DLVO Theory

The stability of colloidal particles in the solution can be more explained by using the DLVO theory, which dependent upon its total potential energy. The potential energy (V_T) is the balance of several competing contribution:

$$V_T = V_A + V_R + V_S \tag{2.6}$$

Where V_A is the attraction force

V_R is the repulsion force

V_s is the potential energy due to the solvent

DLVO theory is the theory which involves the stability of colloidal system by using the estimations of the sum of attraction energy (V_A, van der Waals forces) and the energy of repulsion that exist between particles (V_R, overlapping of electrical double layers), in term of distance between particles as shown in Figure 6. The net interaction energy, also known as the energy barrier [26]. However, if the particles are forces with sufficient energy to overcome this energy barrier, the approaching particles would come into contact. Hence, if the sufficiently repulsion energy of particles exist, the dispersion of colloidal solution will resist, and the colloidal system will be stable. On the other hand, if the repulsion mechanism does not exist, or the repulsion energy does not sufficient, then coagulation or flocculation will occur [27].

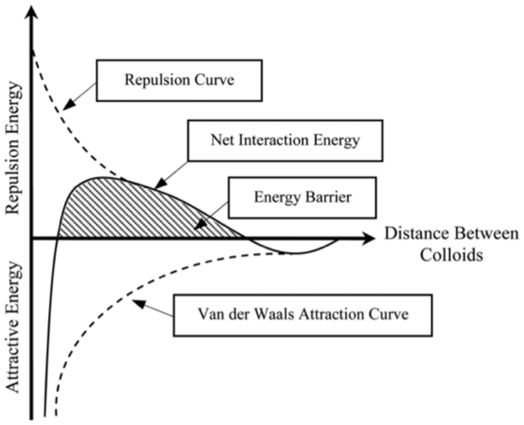

Figure 6. Interparticle forces as a function of interparticle distance

Normally, under the normal conditions, the barrier height (net interaction energy) is much larger than the average thermal energy of the particles. Therefore, the colloidal particles in the solution will remain stable. However, the increasing of the temperature is one of the factors which using to pull them into contact by increasing the kinetic energy to overcome the energy barrier, then the particles will coalesce [26, 27].

2.3.2 Coagulation-Flocculation mechanisms

In coagulation-flocculation process, the small suspension colloids in water are destabilized by the addition of coagulants with an opposite charge for reducing the surface charge of colloids, then the destabilized particles of colloidal system are aggregate and settle, respectively [28]. In addition, for improving the removal or settlement efficiency, the polymeric flocculants with flexible long chain are added after coagulation as coagulant aids. Nevertheless, for the use of polymeric flocculants which act as bridge to connect the particles to form larger flocs, it requires the effective polymers which capable to be adsorbed on the particle surface either by chemical bonding (chemisorption) or physical attachment (physisorption), resulted in the easily remove by sedimentation process [29], as shown in Figure 7.

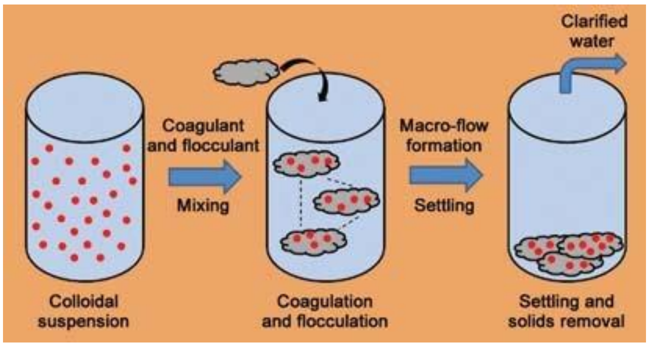

Figure 7. An overview of Coagulation-Flocculation process

For removing of the contaminated metal ions or other suspended colloids in wastewater, and improving the settling time, therefore destabilization process is required. In addition, on the basis of coagulation-flocculation effects, when the kinetic energy of the particles is large enough or overcome the net interaction energy (energy barrier), hence the reduction of the long-range repulsion force between particles which bring the destabilization process occurs, and the particles will enable to aggregate by van der Walls forces, respectively. As a result of the addition of coagulants or flocculants, four mechanisms can bring upon the destabilization and aggregation processes, including charge neutralization, sweep coagulation, bridging, and patch flocculation, which can be achieved with one or a combination of two or more of the mechanisms [29].

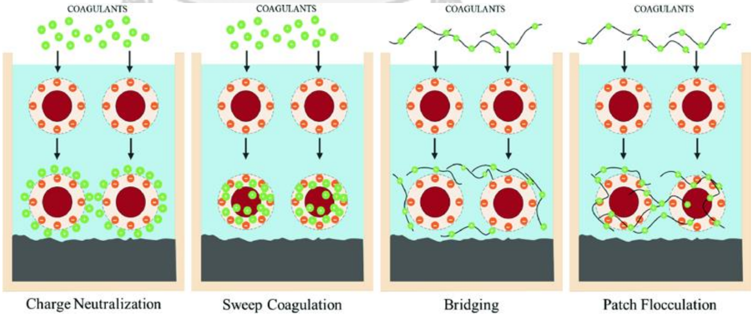

Figure 8. Coagulation-Flocculation mechanisms

As shown in Figure 8, which shows the main mechanisms of coagulation-flocculation process. For the first one is the “charge neutralization” mechanism which resulted from the addition of coagulants with a high positive charge to adsorb on the surface of negative charged particles or colloids. Moreover, when the metal coagulants which normally are trivalent inorganic metal salts, was added to the water at a sufficiently high concentration, so the precipitation of amorphous metal hydroxide ($M(OH)_3$) will occur, and colloid particles can be enmeshed with these precipitates, it is called “sweep coagulation”. Additionally, for the using of polymeric flocculants then “bridging” mechanism is also one of the widely acceptable mechanisms, which can adsorb more than one particle, or link the particles together. However, the performance of polymeric flocculants for improvement the removal or settling efficiency by bridging mechanism, is also dependent upon the isoelectric point, or the molecular weight (MW) of polymers. For the last mechanism is “patch flocculation”, which used polymers or other flocculants with high cationic charge density (>0.15) to adsorb onto an opposite charge of particle surface. However, if the polymeric flocculants have a low cationic charge density (<0.15), then the bridging mechanism would prefer to occur [30, 31].

However, the coagulation-flocculation mechanisms are determined by the coagulants-flocculants selection, dosage of chemicals, and wastewater characteristics etc. Moreover, the majority of chemical additives which can destroy the relative stability of charged between particles, can be categorized into two categories including hydrolyzing metal coagulants, which are normally used aluminum or ferric metal salts, and organic polymeric flocculants which can be both of synthetic- or bio- polymers (cationic (+), anionic (-), amphoteric (+/-), and nonionic), that will be more fully described in the next following subsection [32-34].

2.3.3 Coagulation-Flocculation reagents (coagulants/ flocculants)

The consideration and selection of coagulant/ flocculant chemicals must be dependent upon the type of suspended solid to be removed, raw water condition, cost of chemical, technique, effluent quality, and cost of dose required for effective treatment etc. Furthermore, for the common chemical reagents which including inorganic metal coagulants, such as aluminum and ferric salts, and organic polymeric flocculants which mainly include synthetic- and bio- polymers. However, nowadays a number of reports were utilized a combination of inorganic metal coagulants and organic polymeric flocculants for improvement the capability of colloids removal by coagulation-flocculation process [32].

2.3.3.1 Inorganic Coagulants

Inorganic coagulants are typically divalent (M^{2+}) or trivalent (M^{3+}) metal salts which can be rapidly hydrolyzed in water to form cationic species and adsorb on the negatively charged suspended colloids (charge neutralization), resulting in the reduction of surface charges (destabilization process). Furthermore, the commonly used inorganic coagulants can be categorized into two categories based on: aluminum (Al) or iron (Fe) compounds, which are the most commonly used coagulants because of their commercially, availability, and relatively low-cost reagents [32].

In addition, the insoluble reaction products which converted the soluble arsenic species from wastewater by the addition of metal salts (inorganic coagulants) can occur through three mainly mechanisms including (i) precipitation of iron arsenate ($FeAsO_4$), (ii) coprecipitation between arsenic species and metal hydroxides, and (iii) adsorption on soluble arsenic species onto the solid hydroxide precipitates, which shown in Figure 9.

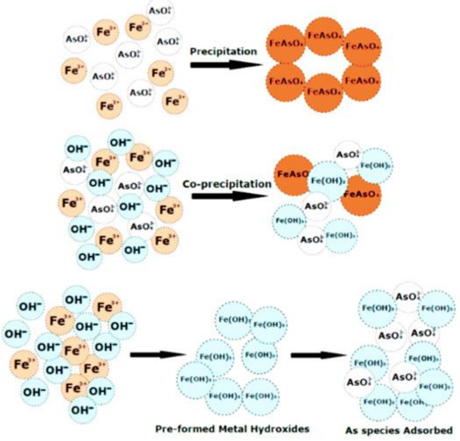

Figure 9. Mechanisms of arsenic removal using metal ions

However, the use of inorganic metal salts as coagulants also exhibited several disadvantages especially aluminum compounds which may have the adverse effects on environment and human health, for example, Alzheimer’s disease. Moreover, the environmentally friendly inorganic metal salts, such as titanium (Ti) or magnesium (Mg), are another important class of inorganic coagulants which can be used in a combination with the conventional metal coagulants for improvement the removal or settling efficiency, and also resulted in the enhancement of sludge dewaterability [33].

The advantages and disadvantages of commonly inorganic coagulants which are mentioned above, are also summarized in Table 2.9 [32, 33].

Table 2.8 Inorganic metal coagulants and their advantages-disadvantages

Metal coagulants	Advantages	Disadvantages
Aluminum salts **($Al_2(SO_4)_3$)**	- Relatively low cost - Simple in operation - Effective over wide range of pH - Alum flocs are larger and more compact than ferric flocs	- Produces toxic sludge - Low removal of (As(III)) - Pre-oxidation step required - Poorer dewatering performance of alum sludge than ferric sludge at high pH
Ferric salts **($Fe_2(SO_4)_3$, $FeCl_3$)**	- Commercially chemicals - More effective than aluminum at high pH and doses - Ferric is lower toxicity than aluminum	- Medium removal of As(III) - Sedimentation and filtration needed
Others **(Ti/ Mg etc.)**	- Flocs size in a combination of some divalent metal (M^{2+}) with the conventional coagulants (Al/ Fe) are larger than the using of the only conventional conditioners, resulted in an enhancement of dewaterability.	- Usually expensive than the conventional or traditional coagulants (Al/ Fe)

Conversely, the use of inorganic metal salts as coagulants in coagulation process also has some disadvantage; for example, it can produce large amount of sludge which can cause the potential toxicity to environment, human health, or other living organisms.

Alternatively, the use of organic polymeric flocculants which can be either synthetic- or natural- polymers (cationic (+), anionic (-), amphoteric (+/-), and nonionic), as flocculants or coagulant aids in flocculation process also have the useful properties over inorganic salts, such as the large flocs formation that resulted in the high settling properties [33].

2.3.3.2 Organic Flocculants

Typically, the chemicals used for flocculation process are macromolecular, which can be classified into two main categories, which are synthetic polymers (non-biodegradable), and natural- or bio- polymers (biodegradable). Moreover, on the basis of different monomeric units which contain various types of charges, they can be categorized as nonionic, cationic (+), anionic (-), and amphoteric or ampholytic (+/-) polymers, with variable charge density, as shown their typical structures in Figure 10 [33].

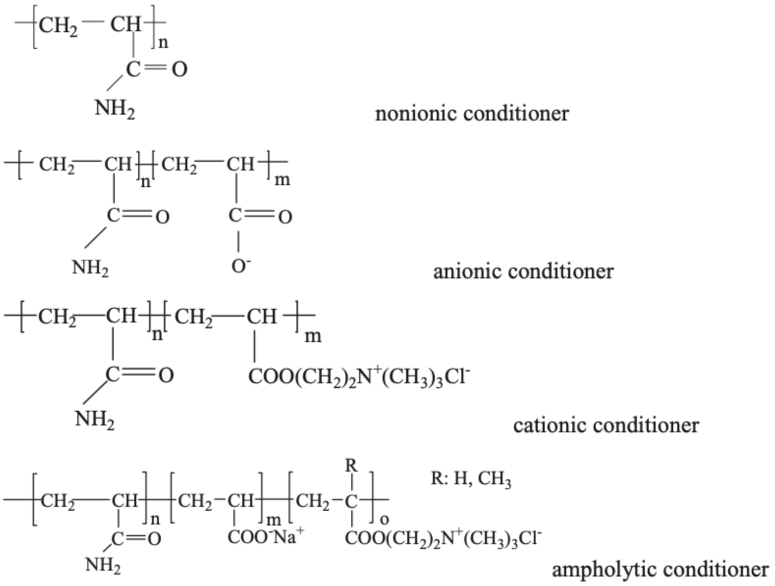

Figure 10. Typical structure of various polymeric conditioners

Nowadays, polymers with long chain and high molecular weight properties, are becoming more widely used either alone, or in a combination with traditional coagulants (aluminum or ferric salts) to attract suspended colloidal particles via mainly mechanisms, which are charge neutralization and bridging mechanisms. Even though the organic polymers are effective over a wide range of pH, produce smaller volumes of more concentrated sludge, and rapidly settling flocs than traditional inorganic coagulants, but the organic polymers also more expensive than the inorganic ones [33].

Furthermore, the flocculation process can occur by various flocculants or coagulant aids by several mechanisms, that were summarized and shown their objectives for each type of flocculants in Table 2.10 (synthetic polymers) [33-35].

Table 2.9 Some synthetic polymer and their objectives in flocculation process

Types	Objectives	Synthetic polymers
Nonionic polymers	- Adsorption of polymers on surface of colloids (Bridge formation)	- Polyacrylamide (PAM)
Cationic polymers (+)	- Reduce zeta potential (Agglomeration) - Create bridges between groups (Complete coagulation)	- Polyvinylammonium chlorohydrate - Polyethylene amine
Anionic polymers (-)	- Replace the anionic groups (Bridge formation)	- Polyvinylsulfonic acids - Polystyrenesulfonic acids - Partially ionized polyacrylamides - Acrylate-acrylamide copolymer

Moreover, synthetic polymers may also contain unpolymerized monomers and additives which can affect to neurotoxic and carcinogenic for human body. Consequently, the more natural-based polymers are the alternatively for replacing oil-based flocculants. Hence, nowadays a number of biopolymers from natural source are interested as alternative flocculants which probably reduce the toxic of sludge production from coprecipitation process.

In addition, the typically polymers from natural sources, which act as flocculants or coagulant aids were summarized and shown their objectives in Table 2.11 (natural- or bio-polymers) [33, 34].

Table 2.10 Some natural- or bio- polymer and their objectives in flocculation process

Types	Objectives	Natural- or bio- polymers
Nonionic polymers	- Adsorption of polymers on surface of colloid (Bridges formation)	- Starch - Polylactic acids (PLA)
Cationic polymers (+)	- Reduce zeta potential (Agglomeration) - Create bridges between group (Complete coagulation)	- Chitosan
Anionic polymers (-)	- Replace the anionic group (Bridges formation)	- Cellulose - Carboxylmethyl cellulose (CMC) - Alginate - Pectin - k- and l- carrageenan - Xanthan gum
Amphoteric polymers (+,-)	- Reduce zeta potential (Agglomeration) - Create bridges between group (Complete coagulation) - Replace the anionic group (Bridges formation)	- Zwitterionic glycine

Even though the natural- or bio- polymers which have the advantage of biodegradability or toxic-free property, the use of synthetic polymers are also more widespread over the natural ones, due to the fact that they are much cheaper than the polymers made from natural sources.

Lastly, natural-based polymers such as chitosan or alginate, have attracted the most interesting ones due to their unique properties, and their many advantages such as the commonly availability from natural source, and the biodegradability which resulted in the environmentally friendly properties [35, 36].

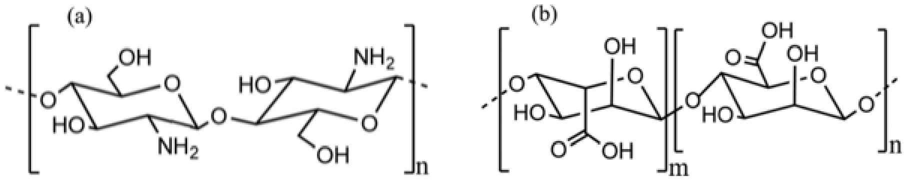

Figure 11. Chemical structure of (a) Chitosan and (b) Alginate

Chitosan (Figure11(a)), is a linear polysaccharide from the deacetylation of chitin, which can be used as flocculants or coagulants depending on pH, and its molecular weight. At slightly acidic conditions, which below the pK_a value ($pK_a = 6.2$), a cationic form of amine groups is presented, and resulting in an electrostatic interaction with other anionic species such as arsenate and phosphate. Conversely, at pH above pK_a value, the chelating or bridging behaviors are occurred [37].

Alginate (Figure11(b)), is a linear biopolymer obtained from marine brown algae, which can exist in the form of anionic species at pH above pK_a value ($pK_a = 3.5$). Nevertheless, the interesting of the nature of alginate is, it can remove the contaminated arsenic or other heavy metal ions by bridging mechanism. Moreover, alginate structure also contains carboxylic groups which can be able to chelate with reactive metal cations, resulting in the usefulness in the wastewater treatment process [38].

2.3.4 Evaluation of various coagulants/ flocculants

A number of kinds of coagulants and flocculants being used today for removing the contaminated suspended colloids in wastewater which mentioned above, including inorganic coagulants and organic flocculants (synthetic- or natural- polymers) were evaluated in this subsection. Due to the fact that inorganic coagulants are cheap and also have good effects on wastewater treatment process. In the same way, the synthetic polymeric flocculants are also the most commonly used because they are excellent in the terms of flocs size formation. But on the other hand, both of inorganic coagulants and synthetic polymeric flocculants are also have many drawbacks, such as the biological toxicity of their residual metal ions and their residual monomers from inorganic metal salts and synthetic polymers, respectively [39].

Thus, nowadays they are many compounds such as natural- or bio- polymers, which being used to study alone or in a combination with traditional metal coagulants, either to replace or reduce the dosage of metal salts and synthetic polymers which act as coagulants and flocculants, consecutively. However, generally driven of the interesting in the used of other compounds instead of the conventional metal coagulants and synthetic polymeric flocculants including, effective removal performance, less toxic sludge production, and their independent of pH condition properties [39, 40].

For improving the arsenic removal performance, cost effectiveness, biodegradability and low toxicity from sludge production, hence the coprecipitation techniques which use mixed metal salts as coagulants, or the use of mixed metal salts as coagulants (coagulation) combined with biopolymers such as chitosan or alginate, as flocculants (flocculation) to form the larger particles and allow to settle by themselves have been interested.

2.3.5 Effect of operating parameters of coagulation-flocculation

For investigation the removal capacity of each coagulant, flocculant, or in the combinatorial system of coagulant and flocculant in coagulation-flocculation process. The effect of various parameters including pH, coagulants or flocculants dosage, and mixing time, were studied for improving their removal efficiency or getting more effective wastewater treatment process [41, 42].

2.3.5.1 pH

In the solution, the acid-base condition is one of the most important factors which effect to surface charge (zeta potential) of metal ions which act as coagulants. Moreover, the pH condition not only affects the zeta potential of metal coagulants, but it also affects the zeta potential of colloidal particles which resulting in the stabilization properties of the colloidal suspension system, as shown in Figure 12. Besides, the solubility and structural changes that occur due to the ionization effect of polymers are also influenced by the pH value [41]. Therefore, the optimum pH condition of water treatment process was essential to specifically investigate for each type of coagulant.

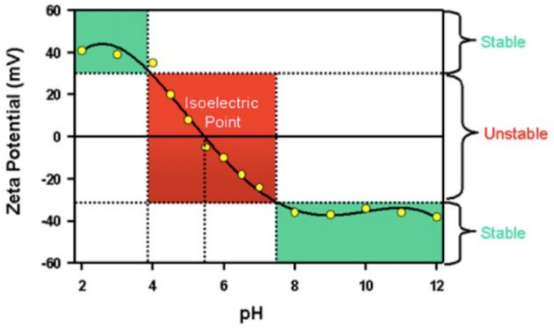

Figure 12. The plot of zeta potential versus pH

From Figure 12 (the plot of zeta potential vs pH of the solution) as shown above. Herein, the zeta potential curve will be positive and negative, at low and high pH, consecutively. Moreover, for the point where the plot showing the zero of zeta potential, it is called “Isoelectric point”. Normally, isoelectric point is the point that occurred from the charge neutralization mechanism, where the colloidal system is least stable and resulting in the destabilization and aggregation processes of particles [41].

2.3.5.2 Dosage

Optimum dosage of coagulants and flocculants are defined as a significant parameter that have been considered for effective coagulation-flocculation performance. Generally, insufficient dosage or overdosing would result in the terrible performance in the treatment process, due to the insufficient ionic strength for the inadequate system, or resuspension of aggregated particles for the overabundant system. Therefore, it is crucial to consider and determine the optimum dosage of coagulants-flocculants in order to minimize the cost of chemical dosing while the effective removal performance in the treatment system can be obtained. Furthermore, the optimum dosage of coagulants-flocculants not only reduce the dosing cost of chemicals, but it can also reduce the toxic sludge formation which resulted in the more environmentally friendly treatment system [42].

2.3.5.3 Mixing time

Besides the effects of pH and coagulants-flocculants dosage, the other crucial factors that affect to the removal efficiency and the flocs formation in flocculation process, is about mixing time. For the longer of mixing time, it can lead to the increasing of flocs breakage, which resulting in the deceasing of flocculation rate. Conversely, if the mixing time is too short, the insufficient collisions can lead to the poor precipitate suspended solids or flocs formation in treatment system [42].

2.4 Literature review

Arsenic removal from water was achieved by various technologies as mentioned above. Nevertheless, each technology has advantages and disadvantages especially concerning efficiency and cost. Coprecipitation or coagulation-flocculation is considered to be a prevailing method which is still widely used due to the fact that it is relatively simple and cost effective for wastewater treatment process from industrial application. Among the available chemical, ferric or aluminum salts have proven to be efficient coagulants for arsenic removal. However, the general trend for water treatment process is to use as less of chemical and energy as possible for reducing the cost and the production of sludge [43]. Therefore, many researchers have found and focused on alternative techniques which used low cost and low dosage of coagulants, such as mixed metal salts ($M^{2+}M^{3+}$) system. For another popular adaptation for reducing the toxic sludge production and the dosage of coagulants needed is, the use of natural- or bio- polymers as flocculants which are generally less toxic, more environmentally friendly, and abundant than synthetic polymeric flocculants.

2.4.1 Arsenic removal by coprecipitation method

Yongfeng et al. (2011) developed a two-step coprecipitation process for arsenic removal by using iron (Fe-As-Fe), or using iron and aluminum (Fe-As-Al) as coagulants. Moreover, not only the efficiency of arsenic removal was investigated, but the stability of coprecipitates was also studied. This two-step coprecipitation process involved an initial mole ratio of Fe/As = 2 at pH7, then it followed by addition of iron (Fe/As = 2) or aluminum (Al/As = 1.5 or 2) as the second step at pH 4. The result of the coprecipitates from two-step coprecipitation process showed higher stability of arsenic-bearing solid waste than traditional which using Fe/As = 4 coprecipitates under one-step coprecipitation. In addition, for the second step which using aluminum as coagulant has more efficiency in terms of generated or enhanced the stability of solid waste than using iron [44].

Chee et al. (2016) studied about coagulation-flocculation process which is widely used for treatment the contaminated wastewater. Nowadays, a number of researchers not only research about the traditional inorganic metal salts (ferric or aluminum) as coagulants, but it also studies about the other flocculants or coagulant aids such as pre-polymerized inorganic metal salts or polymers (synthetic or biopolymers), for improving the removal efficiency and the settle velocity time of colloids. Moreover, this study also reported about the overview understanding of the stability of colloidal particles, and the mechanisms of coagulation-flocculation by using DLVO theory, which involves the attraction and repulsion energy in the terms of distance between particles [45].

2.4.2 Arsenic removal by mixed metal ($M^{2+}M^{3+}$)

Junya et al. (2008) studied about the adsorption technology for arsenic removal by using layered double hydroxide (LDH), which become prime candidates for arsenic removal due to their hydrophilic nature and cationic layered structures. This research is focused on the influence of (1) synthesis method (2) particle size (3) M^{2+}/M^{3+} ratio (4) LDH-based hybrids and (5) competition with other anions. The results showed that LDH synthesized using the coprecipitation had higher arsenic removal efficiency than using hydrothermal method. Moreover, M^{2+}/M^{3+} ratio in LDH can influence the removal efficiency. For the influence of particle size, the As(V) adsorption rate was increased with decreasing the adsorbent particle size, but it had no relationship between adsorption capacity and particle size. For LDH based hybrids with polymer, the result showed an excellent for arsenic adsorption and regeneration ability of adsorbents. In addition, the influence of competing anions for arsenic removal on LDH was related to the anion ability. The As(III) adsorption removal was following by this order: $HPO_4^{2-} < SO_4^{2-} < CO_3^{2-} < F^- < Cl^- < Br^- < NO_3^-$. However, the cost for regeneration of adsorbent is one of the important factors, which used for selecting the treatment method. Furthermore, this research also reported about the adsorption capacity of variable types of mixed metal (M^{2+}/M^{3+}). Then, the report showed the effective arsenic removal by using Mg-Fe-Cl system, which can remove arsenite (As(III)) and arsenate (As(V)) about 286.9 and 331.1 mg/g, respectively [46].

Shan-Li et al. (2008) studied about the removal efficiency of arsenate by using coprecipitation method for synthesized Mg/Al-NO_3 LDH at 2:1, 3:1 and 4:1 mole ratio of Mg:Al. The results showed that LDH with different mole ratio of Mg^{2+}: Al^{3+} exhibited significant differences for their arsenate removal efficiency. The arsenic removal efficiency of 2:1, 3:1 and 4:1 LDH were 1.56, 1.08 and 0.36 mmol/g, respectively. In addition, nitrate orientations in their interlayers of LDH also plays a significant role for determining the adsorption mechanism of arsenate. The result showed that 2:1 and 3:1 LDH exhibit higher arsenate adsorption than 4:1 LDH. Thus, it can be concluded that arsenate is only adsorbed on the external surface of 4:1 LDH. Conversely, 2:1 and 3:1 LDH, the interlayer nitrates between hydroxide sheets were also replace by arsenate. [47].

Caporate et al. (2011) described about the factors which affected to arsenate adsorption on Al-Mg and Fe-Mg layered double hydroxide (LDH). Specifically, they examined arsenate adsorption on two LDH as affected by (i) pH (ii) inorganic [nitrate (NO_3), nitrite (NO_2), phosphate (PO_4), selenite (SeO_3), sulphate (SO_4), and organic [oxalate and tartrate]] competing ligands (iii) residence time on desorption by these ligands. The result showed the lower arsenate adsorption was exhibited by increasing ligands concentration in the pH range 4-10. Moreover, the desirable of arsenate adsorption on Al-Mg-LDH was greater amounts than Fe-Mg-LDH [48].

2.4.3 Heavy metal removal by biopolymers

Henry et al. (2017) studied on orthophosphate removal by coagulation-flocculation method. Moreover, this research reported the removal efficiency of orthophosphate by using variable combinatorial of alum, biopolymers (chitosan or alginate), and biomass (Oat Hull). The combination of these coagulants or flocculants were evaluated for single, binary and ternary systems. And the result showed the efficiency of phosphate removal at an optimum value at pH 6-7 by alum (single system), alum- alginate/chitosan/oat hull (binary system), and alum-alginate-chitosan (ternary system) were about 86, 80, 88, 99 and 98%, respectively. By considering the removal efficiency of phosphate, using alum in conjunction with biopolymers, was more effective for ternary system compared with binary or single system. Therefore, it can be concluded that optimum condition of biopolymers or natural polymers can enhance the phosphate removal by charge neutralization and/or bridging mechanisms via coagulation-flocculation process [49].

Dawn et al. (2016) studied about new methods for arsenic removal from the contaminated wastewater. A combination of ferric (Fe(III)) salt as coagulant, with cactus mucilage as flocculant on coagulation-flocculation process was investigated for improving the arsenic removal efficiency. The result showed the using of cactus mucilage as flocculant can improve the arsenic removal efficiency over the system which using only Fe(III) as coagulant for the treatment of arsenic-contaminated wastewater. Furthermore, cactus mucilage not only improve the removal efficiency which removed 75-96% in 30 minutes, but it can also reduce the colloidal suspensions time from 1 week to 3 minutes [50].

According to the literature reviews [44-50], coprecipitation or coagulation-flocculation is one of the most commonly and widely used methods, which used for removal of arsenic or other heavy metal ions from industrial wastewater, due to its simplicity and effectiveness. But this method also had the limitations and challenges, including toxicity and health hazard by inorganic metal coagulants, large amount of toxic sludge production, inefficient removal performance while using only natural- or bio- polymeric flocculants, and ineffectiveness performance for scaling up procedure. Thus, the new regeneration of coagulation or flocculation reagents with their several advantages, were studied and compared to the traditional coagulants for improving their treatment performance and residual metal concentration. Furthermore, from the perspective of coagulation-flocculation process, various inorganic or organic coagulants-flocculants were investigated and combined together to fully make their advantages for improving their removal efficiency.

Therefore, the removal of arsenic in this study is not only treated by the using of one metal or only traditional coagulants such as ferric or aluminum salts (single system), but the removal of arsenic in this study is also studied and treated by the using of the combinatorial of divalent (M^{2+}) and trivalent (M^{3+}) as coagulants or coagulant aids which is called mixed metals system (binary system) [51]. Moreover, the combination or the synergistic effect between mixed metals ($M^{2+}M^{3+}$) and biopolymers, such as chitosan or alginate system (ternary system) is also studied and investigated to provide the optimum condition for effective arsenic removal [52], via coagulation and flocculation processes.

CHAPTER III

EXPERIMENTAL

3.1 Instruments

The instruments used in this research are shown in Table 3.1

Table 3.1 List of instruments

Instruments	Model, Manufacturing company
Inductively coupled plasma optical emission spectrometer (ICP-OES)	iCAP 6500 DUO, Thermo Scientific
pH/mV meter	FiveEasy Plus, Mettler Toledo
Hot plate magnetic stirrer	SM-15 5plate, AHN myLab
Centrifuge	CENTAUR 2, Sanyo
X-ray diffraction spectrometer (XRD)	DMAX 2200 Ultimate+, Rigaku

The inductively coupled plasma optical emission spectrometer (ICP-OES) was mainly used to determine the remaining of arsenic concentration, or arsenic removal efficiency. The operated conditions of ICP-OES in this research are shown in Table 3.2.

Table 3.2 Conditions of ICP-OES for arsenic determination

Conditions	Values
Arsenic emission wavelength	189.0, 200.3 (nm)
Plasma view	Axial
Ratio frequency power	1150 (W)
Auxiliary gas flow	0.5 (L/min)

Nebulizer gas flow	0.6 (L/min)
Coolant gas flow	12 (L/min)
Flush pump rate	50 (rpm)
Repeatability	3 (replicates)

3.2 Chemicals

All chemicals used in this work were analytical reagent (AR) grade, and they are listed in Table 3.3.

Table 3.3 List of chemicals

Chemicals	**Supplier**
Sodium (meta) arsenite, $NaAsO_2$	Sigma-Aldrich
Sodium arsenate dibasic heptahydrate, Na_2HAsO_4	Sigma-Aldrich
Ferric Chloride anhydrous, $FeCl_3$	Sigma-Aldrich
Aluminum Chloride, $AlCl_3 \cdot 6H_2O$	Sigma-Aldrich
Magnesium Chloride, $MgCl_2 \cdot 6H_2O$	Ajax Finechem
Calcium Chloride anhydrous, $CaCl_2$	Sigma-Aldrich
Chitosan (medium MW)	Sigma-Aldrich
Alginate (medium MW)	Sigma-Aldrich
Sodium hydroxide, NaOH	Merck
Hydrochloric acid 37%, HCl	Merck
Nitric acid 65%, HNO_3	Merck
Acetic acid, CH_3COOH	Merck

3.3 Solution preparation

Most of the solution used in this research were dissolved in deionized (DI) water, except chitosan which was dissolved in 1% of acetic acid (CH_3COOH). Moreover, this research can be separated into two parts including mixed metal systems, which used laboratory or emulated industrial chemicals, and mixed metal combined with biopolymer systems, consecutively. Arsenic concentrations was assigned to be around 300 mg/L due to the fact that the arsenic content in industrial wastewater samples from our previous works and the information from the petrochemical company was in the range of 300 mg/L. This included both As(III) and As(V) in a ratio of 80: 20 percent by weight. Thus the ratio of 4As(III): 1As(V) with the total concentration of 300 mg/L was used for the preparation of simulated wastewaters.

3.3.1 Mixed metal systems

3.3.1.1 Laboratory chemicals

Table 3.4 Solution preparation (Laboratory chemicals)

Stock solution	Concentration	Preparation:
$NaAsO_2$	0.004 M (~300 mg/L)	0.52 g $NaAsO_2$ in 1 L of DI water
$FeCl_3$	0.5 M	8.12 g $FeCl_3$ in 100 mL of DI water
$AlCl_3 \cdot 6H_2O$	0.5 M	12.07 g $AlCl_3 \cdot 6H_2O$ in 100 mL of DI water
$MgCl_2 \cdot 6H_2O$	0.5 M	10.17 g $MgCl_2 \cdot 6H_2O$ in 100 mL of DI water
$CaCl_2$	0.5 M	5.55 g $CaCl_2$ in 100 mL of DI water
NaOH	0.5 M	2 g NaOH in 100 mL of DI water
	1 M	4 g NaOH in 100 mL of DI water
37% HCl	0.5 M	4 mL HCl in 100 mL of DI water
	1 M	8 mL HCl in 100 mL of DI water
65% HNO_3	2% (v/v)	3 mL HNO_3 in 100 mL of DI water

3.3.1.2 Emulated industrial chemicals

Table 3.5 Solution preparation (Emulated industrial chemicals)

Stock solution	Conc./ Mole ratio	Preparation:
Simulated wastewater (4As(III): 1As(V))	0.004 M (~300 mg/L)	0.52 g $NaAsO_2$ in 1 L of DI water 1.25 g Na_2HAsO_4 in 1 L of DI water
$FeCl_3$	2.5 M	40.6 g $FeCl_3$ in 100 mL of DI water
Mg: Fe mixed metal	0.5:1	2.5 g $MgCl_2 \cdot 6H_2O$ in 10 mL of 2.5 M $FeCl_3$
	1:1	5.0 g $MgCl_2 \cdot 6H_2O$ in 10 mL of 2.5 M $FeCl_3$
	1.5:1	7.5 g $MgCl_2 \cdot 6H_2O$ in 10 mL of 2.5 M $FeCl_3$
	2:1	10.0 g $MgCl_2 \cdot 6H_2O$ in 10 mL of 2.5 M $FeCl_3$
Ca: Fe mixed metal	0.5:1	2.8 g $CaCl_2$ in 10 mL of 2.5 M $FeCl_3$ (heat)
	1:1	5.6 g $CaCl_2$ in 10 mL of 2.5 M $FeCl_3$ (heat)
	1.5:1	8.4 g $CaCl_2$ in 10 mL of 2.5 M $FeCl_3$ (heat)
	2:1	11.2 g $CaCl_2$ in 10 mL of 2.5 M $FeCl_3$ (heat)
NaOH	0.5 M	2 g NaOH in 100 mL of DI water
	1 M	4 g NaOH in 100 mL of DI water
	2.5 M	10 g NaOH in 100 mL of DI water
37% HCl	0.5 M	4 mL HCl in 100 mL of DI water
	1 M	8 mL HCl in 100 ml of DI water
	2.5 M	20 mL HCl in 100 ml of DI water
65% HNO_3	2% (v/v)	3 mL HNO_3 in 100 mL of DI water

3.3.2 Combination of mixed metal and biopolymer systems

Table 3.6 Solution preparation (Mixed metal combine with biopolymer)

Stock solution	Conc./ Mole ratio	Preparation:
Simulated wastewater (4As(III): 1As(V))	0.004 M (~300 mg/L)	0.52 g $NaAsO_2$ in 1 L of DI water 1.25 g Na_2HAsO_4 in 1 L of DI water
$FeCl_3$	2.5 M	40.6 g $FeCl_3$ in 100 mL of DI water
Mg: Fe mixed metal	0.5:1	2.5 g $MgCl_2 \cdot 6H_2O$ in 10 mL of 2.5 M $FeCl_3$
Ca: Fe mixed metal	0.5:1	2.8 g $CaCl_2$ in 10 mL of 2.5 M $FeCl_3$ (heat)
Chitosan	2 % (w/v)	2 g chitosan in 100 mL of 1% CH_3COOH
Alginate	2 % (w/v)	2 g alginate in 100 mL of DI water
NaOH	0.5 M	2 g NaOH in 100 mL of DI water
	1 M	4 g NaOH in 100 mL of DI water
	2.5 M	10 g NaOH in 100 mL of DI water
37% HCl	0.5 M	4 mL HCL in 100 ml of DI water
	1 M	8 mL HCL in 100 ml of DI water
	2.5 M	20 mL HCL in 100 ml of DI water
65% HNO_3	2% (v/v)	3 mL HNO_3 in 100 mL of DI water
CH_3COOH	1% (v/v)	1 mL CH_3COOH in 100 mL of DI water

3.4 Batch experimental for arsenic removal by coprecipitation method

3.4.1 Mixed metal systems

Figure 13. Schematic procedure of mixed metal system process

3.4.1.1 Laboratory chemicals

As(III) solution (20 mL of 300 mg/L) was stirred (300 rpm) at room temperature with mixed metals solution (M^{2+} and M^{3+} solution) and the pH was adjusted using 1 M NaOH and/or HCl. After the coprecipitation process, the solution was allowed to settle by the gravity or centrifugation technique. Then the solution was filtered by using 0.45 µm nylon syringe filter membrane, and the filtrated solution was analyzed for the arsenic concentration by ICP-OES, as shown in Figure 13.

3.4.1.2 Emulated industrial chemicals

Simulated wastewater, 4As(III): 1As(V) solution (100 mL of 300 mg/L) was stirred (300 rpm) at room temperature with mixed metals solution ($M^{2+}M^{3+}$ solution) and adjusted the pH by using 2.5 M NaOH and/or HCl. After the coprecipitation process, the solution was allowed to settle by the gravity or centrifugation technique. Then the solution was filtered by using 0.45 µm nylon syringe filter membrane, and the filtrated solution was analyzed for the arsenic concentration by ICP-OES, as shown in Figure 13.

3.4.2 Combination of mixed metal and biopolymer systems

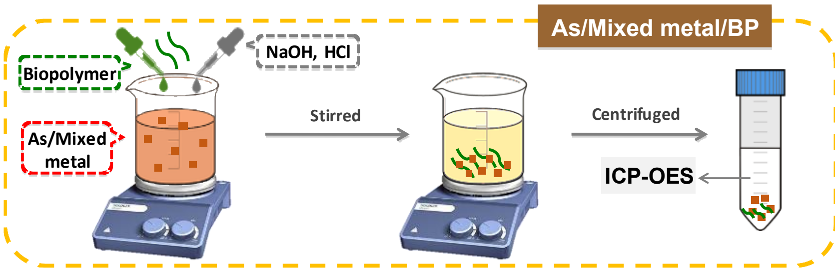

Figure 14. Schematic procedure of mixed metal combine with biopolymer system process

Simulated wastewater, 4As(III): 1As(V) solution (20 mL of 300 mg/L) was stirred (300 rpm) at room temperature with mixed metals solution ($M^{2+}M^{3+}$ solution) and adjusted the pH by using 2.5 M NaOH and/or HCl. Then, biopolymer (alginate or chitosan) was added into the As/mixed metal hydroxide colloidal solution. After the coprecipitation process, the solution was allowed to settle by the gravity or centrifugation technique. Then the solution was filtered by using 0.45 μm nylon syringe filter membrane, and the filtrated solution was analyzed for the arsenic concentration by ICP-OES, as shown in Figure 14.

All experiments were performed in triplicate. Then the efficiency of arsenic removal was calculated from the following equation:

$$\text{Removal efficiency (\%)} \quad = \quad (C_0\text{-}C_e) \,/\, C_0 \quad \times \quad 100 \qquad (3.1)$$

Where C_0 is the initial of arsenic concentration

C_e is the equilibrium of arsenic concentration

Then, the result was evaluated by comparing the arsenic removal efficiency (%) in the different constituents and conditions, to provide the effective treatment system for arsenic contaminated wastewater.

3.5 Optimization for arsenic removal by coprecipitation method

3.5.1 Mixed metal systems

Several parameters of mixed metal system were investigated in laboratory chemicals part, including the effect of pH and M^{2+}: M^{3+} mole ratio of mixed metal (MgFe, CaFe, MgAl, and CaAl) by using 0.004 M (~300 mg/L) as an initial concentration of As(III) solution.

3.5.1.1 Laboratory chemicals

3.5.1.1.1 Effect of pH and M^{2+}: M^{3+} mole ratio

The effect of pH on arsenic removal was studied at pH 7, 9 and 11 by using NaOH and/or HCl to adjust. Moreover, the mole ratio of M^{2+}: M^{3+} (MgFe, CaFe, MgAl and CaAl) at 2:1, 3:1 and 4:1 was varied by using 2.5:1 of Fe: As mole ratio, 300 rpm for speed of stirring, and 0.004 M (~300 mg/L) as an initial concentration of As(III) solution.

Table 3.7 Coprecipitation of arsenic with mixed metal at various M^{2+}: M^{3+} mole ratio (Laboratory chemicals)

pH	$NaAsO_2$ (mL)	M^{2+}: M^{3+}	M^{3+} (mL)	M^{2+} (mL)	H_2O (mL)
7, 9, 11	20	2: 1	0.4	0.8	0.8
		3: 1	0.4	1.2	0.4
		4: 1	0.4	1.6	-

Furthermore, a number of parameters of mixed metal systems were also investigated in emulated industrial chemicals part, including the effect of M^{2+}: M^{3+} mole ratio, $M^{2+}M^{3+}$: As mole ratio, step of pH adjustment, retention time and speed of stirring, by using 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

3.5.1.2 Emulated industrial chemicals

3.5.1.2.1 Effect of pH and M^{2+}: M^{3+} mole ratio

The effect of pH on arsenic removal was studied at pH 7, 9 and 11 by using NaOH and/or HCl to adjust. Moreover, the mole ratio of M^{2+}: M^{3+} (MgFe or CaFe) at 0.5:1, 1:1, 1.5:1 and 2:1 was varied by using 2.5:1 mole ratio of Fe: As, 300 rpm for speed of stirring, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

Table 3.8 Coprecipitation of arsenic with mixed metal at various M^{2+}: M^{3+} mole ratio (Emulated industrial chemicals)

pH	$NaAsO_2$ + Na_2HAsO_4 (mL)	M^{2+}: M^{3+}	$M^{2+}M^{3+}$ (mL)
7, 9, 11	100 (4As(III): 1As(V))	0.5: 1	0.4
		1: 1	0.4
		1.5: 1	0.4
		2: 1	0.4

3.5.1.2.2 Effect of pH and $M^{2+}M^{3+}$: As mole ratio

The effect of pH on arsenic removal was studied at pH 7, 9 and 11 by using NaOH and/or HCl to adjust. Moreover, the mole ratio of $M^{2+}M^{3+}$: As (MgFe: As and CaFe: As) at 1.25:1, 1.5:1, 2:1 and 2.5:1 was varied by using 0.5:1 mole ratio of M^{2+}: M^{3+}, 300 rpm for speed of stirring, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

Table 3.9 Coprecipitation of arsenic with mixed metal at various $M^{2+}M^{3+}$: As mole ratio (Emulated industrial chemicals)

pH	$NaAsO_2 + Na_2HAsO_4$ (mL)	$M^{2+}M^{3+}$: As	$M^{2+}M^{3+}$ (mL)
7, 9, 11	100 (4As(III): 1As(V))	1.25: 1	0.15
		1.5: 1	0.18
		2.0: 1	0.24
		2.5: 1	0.31

3.5.1.2.3 Effect of step of pH adjustment

The effect of step of pH adjustment (continuous, metal pre-added, acid/base pre-added) on arsenic removal was studied, by using 0.5:1 mole ratio of Mg: Fe with 1.25:1, 1.5:1, 2:1 and 2.5:1 mole ratio of MgFe: As, 300 rpm for speed of stirring at pH 9, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

3.5.1.2.4 Effect of retention time

The effect of retention time (0, 15, 30 and 60 minutes) on arsenic removal was studied, by using 0.5:1 mole ratio of Mg: Fe with 2.5: 1 mole ratio of MgFe: As, and 300 rpm for speed of stirring at pH 9, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

3.5.1.2.5 Effect of speed of stirring

The effect of speed of stirring (0, 300, 400, 500, 600, 700 and 800 rpm) on arsenic removal was studied, by using 0 minute of retention time and 0.5:1 mole ratio of Mg: Fe with 2.5: 1 mole ratio of MgFe: As, at pH 9, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

3.5.1.3 Removal efficiency by mixed metal system under optimal condition

The arsenic removal efficiency of mixed metal (MgFe and CaFe) systems with an optimum condition (metal pre-added as a step of pH adjustment with 0 minute for retention time, and 400 rpm for speed of stirring) at pH 7, 9 and 11 was evaluated, by using 0.5:1 mole ratio of M^{2+}: M^{3+} with 1.25:1, 1.5:1, 2:1 and 2.5:1 mole ratio of $M^{2+}M^{3+}$: As, and 0.004 M (~300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

Moreover, several parameters of the combination of mixed metal and biopolymer systems were also studied for improving the arsenic removal efficiency and/or settling velocity performance. The effect of biopolymer including type, concentration, retention time, and pH solution of the combination between mixed metal and biopolymer system were also investigated, by using 0.004 M (300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V).

3.5.2 Combination of mixed metal and biopolymer systems

3.5.2.1 Effect of biopolymer concentration and retention time

Table 3.10 Coprecipitation of arsenic with mixed metal and biopolymer at various concentration

pH	$NaAsO_2$ + Na_2HAsO_4 (mL)	Mixed metal system	$M^{2+}M^{3+}$: As	Biopolymer conc. (%w/v)	Biopolymer (mL)
9	20 (4As(III): 1As(V))	MgFe or CaFe	1.25: 1	0.3	2.4
				0.5	4.0
				0.7	5.6
				0.9	7.2

3.5.2.1.1 Mixed metal with alginate (ALG) system

The synergistic effect of mixed metal (MgFe or CaFe) combining with alginate at various concentration (0.3, 0.5, 0.7 and 0.9%w/v) and retention time (5, 15, 30 and 60 minutes) for arsenic removal was studied, by using 0.5:1 mole ratio of M^{2+}: M^{3+} (Mg: Fe and Ca: Fe), and 1.25: 1 mole ratio of $M^{2+}M^{3+}$: As (MgFe: As and CaFe: As) at pH 9 with metal pre-added as a step of pH adjustment and 400 rpm for speed of stirring, by using 0.004 M (300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V).

3.5.2.1.2 Mixed metal with chitosan (CTS) system

The synergistic effect of mixed metal (MgFe or CaFe) combining with chitosan at various concentration (0.3, 0.5, 0.7 and 0.9%w/v) and retention time (5, 15, 30 and 60 minutes) for arsenic removal were studied, by using 0.5:1 mole ratio of M^{2+}: M^{3+} (Mg: Fe and Ca: Fe), and 1.25: 1 mole ratio of $M^{2+}M^{3+}$: As (MgFe: As and CaFe: As) at pH 9 with metal pre-added as a step of pH adjustment and 400 rpm for speed of stirring, by using 0.004 M (300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V).

3.5.2.2 Effect of biopolymer at various pH and $M^{2+}M^{3+}$: As mole ratio

Table 3.11 Coprecipitation of arsenic with mixed metal and biopolymer at various pH and $M^{2+}M^{3+}$: As mole ratio

pH	$NaAsO_2$ + Na_2HAsO_4 (mL)	Mixed metal system	$M^{2+}M^{3+}$: As	Biopolymer conc. (%w/v)	Biopolymer (mL)
7,9,11	20 (4As(III): 1As(V))	MgFe or CaFe	1.25: 1 1.5: 1 2: 1 2.5: 1	0.7% ALG	5.6

3.5.2.2.1 MgFe mixed metal with alginate (ALG) system

The synergistic effect of mixed metal (MgFe) combine with biopolymer (alginate) at various pH (7, 9 and 11) and $M^{2+}M^{3+}$: As mole ratio of MgFe: As (1.25: 1, 1.5: 1, 2: 1 and 2.5: 1) were also studied, by using 0.7%w/v of alginate as an optimum type and concentration of biopolymer for MgFe mixed metal system, with metal pre-added as a step of pH adjustment and 400 rpm for speed of stirring, by using 0.004 M (300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V).

3.5.2.2.2 CaFe mixed metal with alginate (ALG) system

The synergistic effect of mixed metal (CaFe) combine with biopolymer (alginate) at various pH (7, 9 and 11) and $M^{2+}M^{3+}$: As mole ratio of CaFe: As (1.25: 1, 1.5: 1, 2: 1 and 2.5: 1) were also studied, by using 0.7%w/v of alginate as an optimum type and concentration of biopolymer for CaFe mixed metal system, with metal pre-added as a step of pH adjustment and 400 rpm for speed of stirring, by using 0.004 M (300 mg/L) as an initial concentration of simulated wastewater, 4As(III): 1As(V).

3.6 Application in real wastewater sample

Real industrial wastewater sample obtained from a petrochemical company. It contains total arsenic in the range of 300-900 mg/L. Firstly, the wastewater was filtered and analyzed for exact concentration of total arsenic by ICP-OES. Then, the wastewater was subjected to the experiment of arsenic removal by using coprecipitation process. Moreover, the coprecipitation process of real wastewater sample was treated by the most effective treatment system with an optimum amount and condition.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Distribution diagram of metal species under different pH conditions

This study deals with the arsenic removal by coprecipitation method with variable combination of well-known inorganic metal salts, such as ferric chloride ($FeCl_3$) or aluminum chloride ($AlCl_3$) which is a good candidate for removing of arsenic, combined with the environmentally friendly inorganic metal salts, such as magnesium chloride ($MgCl_2$) or calcium chloride ($CaCl_2$), which is called “mixed metal system” as coagulants to precipitate or coprecipitate with arsenic from contaminated wastewater.

For better understanding of the metal (Fe^{3+}, Al^{3+}, Mg^{2+} and Ca^{2+}) for arsenic removal process, the metal species on distribution diagram as shown in Figure 15 can assist for understanding and selection of the optimal pH-range conditions for effective arsenic removal treatment process [53-56].

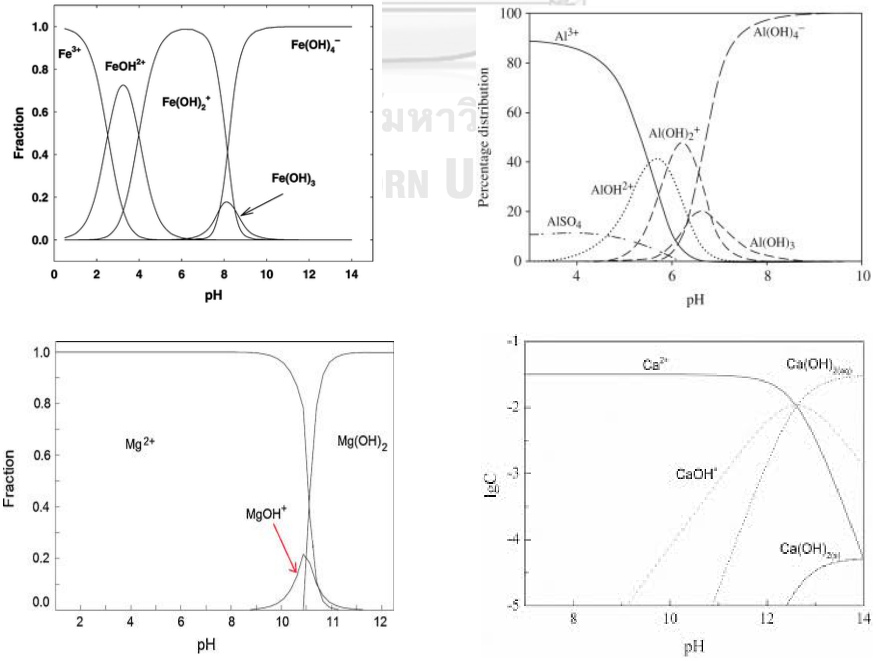

Figure 15. Distribution of Fe^{3+}, Al^{3+}, Mg^{2+} and Ca^{2+}

Therefore, this study interested in the pH range more than 7 because metal hydroxides can easily form over pH 7. Moreover, the pH not only affects to the coagulant (mixed metal) species, but it also plays an important role in species distribution of arsenic (arsenite, As(III) and arsenate, As(V)), that can be determined and explained by their pKa values, as described in the next following paragraphs. For coprecipitation purpose, dissociated species of arsenic or negatively charged arsenic species were preferred.

These various types of metal ion forms, especially metal hydroxide formation of ferric chloride or aluminum chloride which are extensively to be a good candidate for arsenic removal by coprecipitation process, as they have positively charged surface which encourages the removal of negatively charged on arsenic surface by electrostatic attraction. Conversely, as arsenic exists as neutral or uncharged species which is a mainly form of arsenite (As(III)), the electrostatic interaction may not play an important or predominant role for removing of arsenic. Therefore, the ligand exchange mechanism seems to be responsible for arsenic removal by metal hydroxides, which can be represented the probable mechanism for removing of arsenic as follows: [57]

$$\text{M-OH} + H_3AsO_3 \longrightarrow MH_2AsO_3 + H_2O \qquad (4.1)$$

Furthermore, Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) was used to evaluate the remaining amount of arsenic by comparing the arsenic removal efficiency (%) in the different constituents and conditions, to provide the most effective treatment method which applicable for treatment the real industrial wastewater sample.

4.2 Optimization of mixed metal systems for arsenic removal

In coprecipitation process using laboratory chemicals or emulated industrial chemicals, mixed metal salts were added into the simulated wastewater under the efficient stirring, then mixed metal hydroxide micro-flocs were formed. The reaction between metal hydroxides and arsenic could possibly involve the complexation between metal which act as coagulant and arsenic species by ligand exchange mechanism or charged neutralization between anionic species of arsenic and metal hydroxides by electrostatic attraction process.

4.2.1 Laboratory chemicals

Several parameters of mixed metal system were investigated in laboratory chemical part, including the effect of pH and M^{2+}: M^{3+} mole ratio of mixed metal (MgFe, CaFe, MgAl and CaAl) by using 300 mg/L as an initial concentration of simulated wastewater, As(III) solution.

4.2.1.1 Effect of pH and M^{2+}: M^{3+}mole ratio

4.2.1.1.1 MgFe mixed metal system

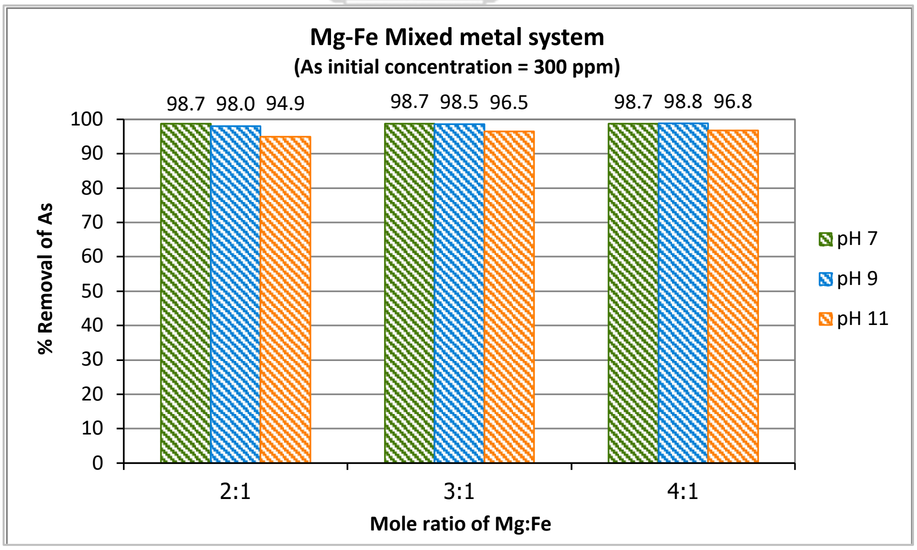

Figure 16. Arsenic removal (%) as a function of mole ratio of Mg: Fe at various pH

The results from Figure 16 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Mg: Fe (2:1, 3:1 and 4:1) by using 2.5:1 of Fe: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of As(III) solution by using MgFe mixed metal system. The results showed that the removal efficiency of arsenic remain constant as increasing of Mg: Fe mole ratio from 2:1 to 4:1, at pH 7 and 9. Conversely, the arsenic removal efficiency slightly increased when increasing the Mg: Fe mole ratio at pH11. However, the removal efficiency of arsenic not significantly changed or effected by changing the pH solution at pH7 and 9, but it slightly decreased at pH11 by using the comparable dosage values of mixed metal.

This could be described by the species distribution of As(III) at pH7-11, the uncharged or neutral form (H_3AsO_3) at pH7, the neutral and deprotonated forms (H_3AsO_3, $H_2AsO_3^-$) at

pH9 present in the solution which favored to coprecipitate with MgFe mixed metal hydroxides. Moreover, the deprotonated or anionic form of arsenite ($H_2AsO_3^-$) at pH9 can be also precipitated with the ionized form of magnesium (Mg^{2+}). On the other hand, when the pH of the solution increased to pH11, the removal efficiency of arsenic a bit decreased probably due to the competition process between anionic species of arsenite and hydroxide ions, which resulting to the lower arsenic removal efficiency at 2:1 and 3:1 mole ratio of MgFe. Whereas the mole ratio of Mg: Fe at 4:1 not effected by changing the pH solution probably due to the increasing of magnesium which resulting to more coprecipitation process between negatively charged of arsenic species and hydroxides form of magnesium.

4.2.1.1.2 CaFe mixed metal system

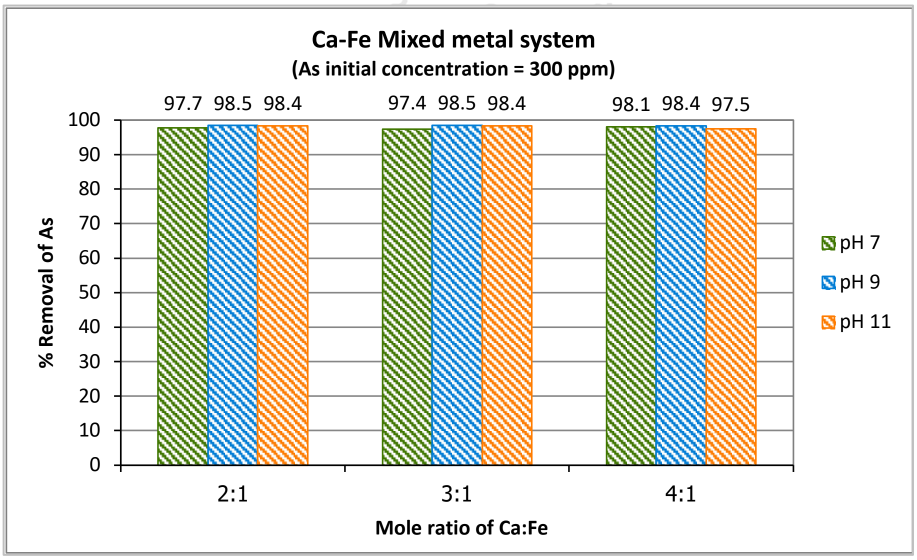

Figure 17. Arsenic removal (%) as a function of mole ratio of Ca: Fe at various pH

The results from Figure 17 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Ca: Fe (2:1, 3:1 and 4:1) by using 2.5:1 of Fe: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of As(III) solution by using CaFe mixed metal system. The results showed that the removal efficiency of arsenic remain constant as increasing of Ca: Fe mole ratio from 2:1 to 4:1, at pH7, 9 and 11. Moreover, the arsenic removal efficiency by using CaFe mixed metal not significantly changed or effected by changing the pH solution.

This could be described by the species distribution of As(III) at pH7-11, the uncharged or neutral form (H_3AsO_3) at pH7, the neutral and deprotonated forms (H_3AsO_3, $H_2AsO_3^-$) at pH9, and the only deprotonated forms ($H_2AsO_3^-$, $HAsO_3^{2-}$) at pH11 present in the solution which favored to coprecipitate with CaFe mixed metal hydroxides. Moreover, the deprotonated forms or anionic species of arsenite at pH9 and 11 can be also precipitated with the ionized form of calcium (Ca^{2+}, $Ca(OH)^+$), which probably resulting to not significantly changed or effected by hydroxide ions competition at pH11.

4.2.1.1.3 MgAl mixed metal system

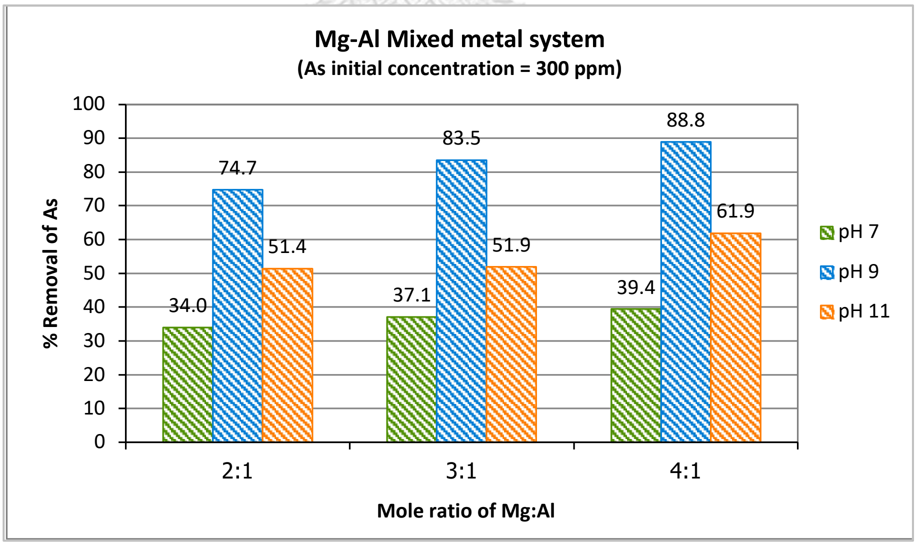

Figure 18. Arsenic removal (%) as a function of mole ratio of Mg: Al at various pH

The results from Figure 18 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Mg: Al (2:1, 3:1 and 4:1) by using 2.5:1 of Al: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of As(III) solution by using MgAl mixed metal system. The results showed that the removal efficiency of arsenic increased as increasing of Mg: Al mole ratio from 2:1 to 4:1, especially at pH9 and 11. Moreover, the arsenic removal efficiency by using MgAl mixed metal also significantly effect by changing the pH solution. Arsenite, As(III) was the most effectively removed at pH9 while the removal efficiency decreased at pH7 and 11 by using comparable dosage values of MgAl mixed metal system.

This could be described by the species distribution of As(III) at pH7-11. At pH7, the arsenic removal efficiency was the lowest removal percentage or removal performance compared with pH9 and 11, probably due to the predominantly neutral species of arsenite (H_3AsO_3), which may not be suitable to coprecipitate with mixed metal hydroxide forms via using aluminum as trivalent metal salts. Whereas at pH11, the arsenic removal efficiency is also lower than at pH9, possibly due to the competition between negatively charged of arsenic species and hydroxide ions in coprecipitation process. However, the mole ratio of Mg: Al is another parameter that affecting to arsenic removal efficiency, especially at pH9 and 11, probably due to the fact of magnesium increasing which resulting to more precipitation or coprecipitation process between negatively charged of arsenic species and the ionized or hydroxides form of magnesium.

4.2.1.1.4 CaAl mixed metal system

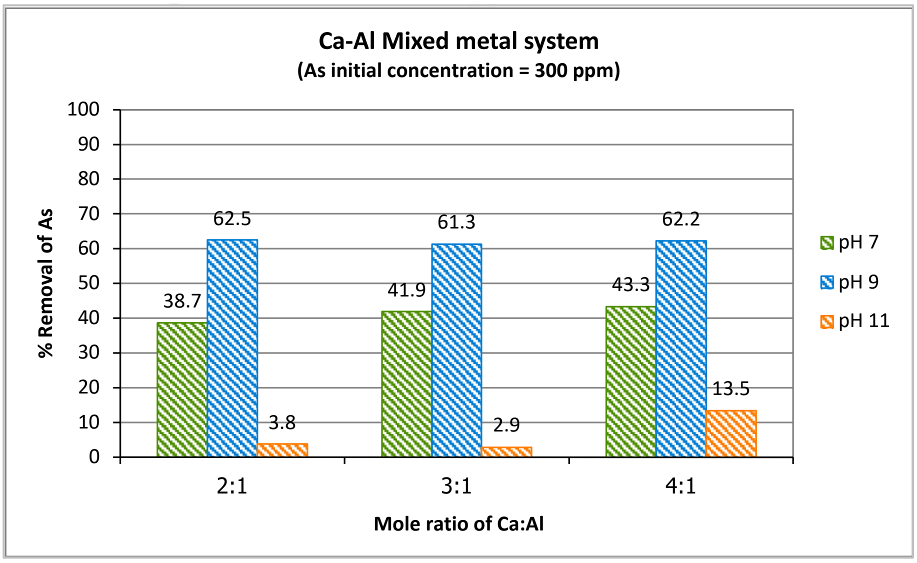

Figure 19. Arsenic removal (%) as a function of mole ratio of Ca: Al at various pH

The results from Figure 19 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Ca: Al (2:1, 3:1 and 4:1) by using 2.5:1 of Al: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of As(III) solution by using CaAl mixed metal system. The results showed that the removal efficiency of arsenic remain constant as increasing of Ca: Fe mole ratio from 2:1 to 4:1, at pH9. Conversely, the arsenic removal efficiency slightly increased when increasing the Ca: Al mole ratio, at pH7 and 11. Moreover, the arsenic removal efficiency by using CaAl mixed metal also significantly effect by changing the pH solution. Arsenite, As(III) was the most effectively removed at pH9, while the removal efficiency decreased at pH7 and 11 by using comparable dosage values of CaAl mixed metal system.

This could be described by the species distribution of As(III) at pH7-11. At pH7, the arsenic removal efficiency was lower than at pH9, possibly due to the predominant neutral species of arsenite (H_3AsO_3) which may not be suitable to coprecipitate with mixed metal hydroxide forms via using aluminum as trivalent metal salts. Whereas at pH11, the arsenic removal efficiency is the lowest removal percentage or removal performance compared with pH7 and 9, probable due to the competition between negatively charged of arsenic species and hydroxide ions to coprecipitate, or the electrostatic repulsion between anionic species of arsenic and negatively charged on metal hydroxide surface, which resulting in insignificantly of arsenic removal percentage. However, the mole ratio of Ca: Al is another parameter that affecting to the arsenic removal efficiency at pH7 and 11, possibly due to the fact of calcium increasing with resulting to more precipitation or coprecipitation process between negatively charged of arsenic species and the ionized forms of calcium (Ca^{2+}, $Ca(OH)^{+}$) at pH11.

Table 4.1 Arsenic removal efficiency using mixed metal system (MgFe, CaFe, MgAl, CaAl) at various pH and M^{2+}: M^{3+} mole ratio (Laboratory chemicals)

As solution (300 mg/L)			%Removal (M^{2+}: M^{3+} ratio)		
	System	pH	2: 1	3: 1	4: 1
As(III)	MgFe	7	98.7 ± 0.0	98.7 ± 0.2	98.7 ± 0.0
		9	98.0 ± 0.2	98.5 ± 0.2	98.8 ± 0.2
		11	94.9 ± 1.1	96.5 ± 0.7	96.8 ± 0.5
	CaFe	7	97.7 ± 0.4	97.4 ± 0.4	98.1 ± 0.0
		9	98.5 ± 0.1	98.5 ± 0.3	98.4 ± 0.1
		11	98.4 ± 0.1	98.4 ± 0.1	97.5 ± 0.6
	MgAl	7	34.0 ± 1.1	37.1 ± 4.6	39.4 ± 5.5
		9	74.7 ± 1.5	83.5 ± 16.3	88.8 ± 7.0
		11	51.4 ± 11.8	51.9 ± 12.8	61.9 ± 0.1
	CaAl	7	38.7 ± 4.6	41.9 ± 3.8	43.3 ± 4.8
		9	62.5 ± 3.2	61.3 ± 1.6	62.2 ± 1.0
		11	3.8 ± 8.6	2.9 ± 7.0	13.5 ± 4.3

A number of parameters of mixed metal system were investigated in laboratory chemical part, including the effect of pH solution and M^{2+}: M^{3+} mole ratio of mixed metal (MgFe, CaFe, MgAl and CaAl). The results showed that mixed metal system which using ferric chloride ($FeCl_3$) as trivalent metal salts was more effectively for arsenic removal than using aluminum chloride ($AlCl_3$) as trivalent metal salts system, because the distribution species of aluminium (Al), especially at pH 11 ($Al(OH_4)^-$) which can cause the electrostatic repulsion to arsenic species ($H_2AsO_3^-$, $HAsO_4^-$), as shown in Table 4.1.

Therefore, a number of parameters of mixed metal systems which using ferric chloride as trivalent metal salts (MgFe, CaFe), were selected to investigate in emulated industrial chemical part as shown in the next following subsections.

4.2.2 Emulated industrial chemicals

Several parameters of mixed metal system which using ferric chloride as trivalent metal salts (MgFe, CaFe) were investigated in emulated industrial chemical part, including the effect of M^{2+}: M^{3+} mole ratio, $M^{2+}M^{3+}$: As mole ratio, step of pH adjustment, retention time, and speed of stirring by using 300 mg/L as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

4.2.2.1 Effect of pH and M^{2+}: M^{3+} mole ratio

4.2.2.1.1 MgFe mixed metal system

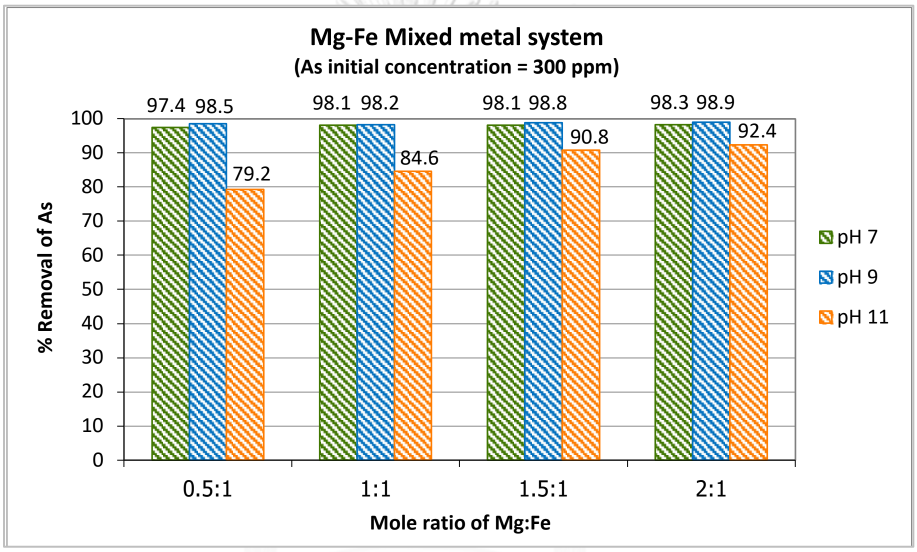

Figure 20. Arsenic removal (%) as a function of mole ratio of Mg: Fe at various pH

This results from Figure 20 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Mg: Fe (0.5:1, 1:1, 1.5:1 and 2:1) by using 2.5:1 of Fe: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system. The results showed that the removal efficiency of arsenic remain constant as decreasing Mg: Fe mole ratio from 2:1 to 0.5:1, at pH7 and 9. Conversely, the arsenic removal efficiency decreased when decreasing of Mg: Fe mole ratio at pH11. Furthermore, the removal efficiency of arsenic not essentially changed or effected by changing the pH of the solution, at pH7 and 9. Nevertheless, the arsenic removal efficiency decreased at pH11 by using the comparable dosage values of mixed metal.

This could be described by the species distribution of As(III) and As(V) at pH7-11, the neutral form of arsenite (H_3AsO_3) or the deprotonated forms of arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$) at pH7, the neutral and deprotonated forms of arsenite (H_3AsO_3, $H_2AsO_3^-$) or the deprotonated form of arsenate ($HAsO_4^{2-}$) at pH9 present in the solution which favored to coprecipitate with MgFe mixed metal hydroxides. Moreover, the deprotonated or anionic form of arsenite ($H_2AsO_3^-$) at pH9, and the deprotonated forms of arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$) at pH7 and 9, can be also precipitated with the ionized form of magnesium (Mg^{2+}). On the other hand, when the pH of the solution increased to pH11, the removal efficiency of arsenic decreased probably due to the competition between negatively charged of arsenic species and hydroxide ions in coprecipitation process, or the electrostatic repulsion between anionic species of arsenic and negatively charged on metal hydroxides surface, which resulting to the lower arsenic removal efficiency for all of Mg: Fe mole ratio at pH11 compared with pH7 and 9. Nevertheless, the mole ratio of Mg: Fe is another parameter that affecting to the arsenic removal performance at pH11, probably due to the increasing of magnesium which resulting to more coprecipitation process between negatively charged of arsenic species and hydroxides form of magnesium.

4.2.2.1.2 CaFe mixed metal system

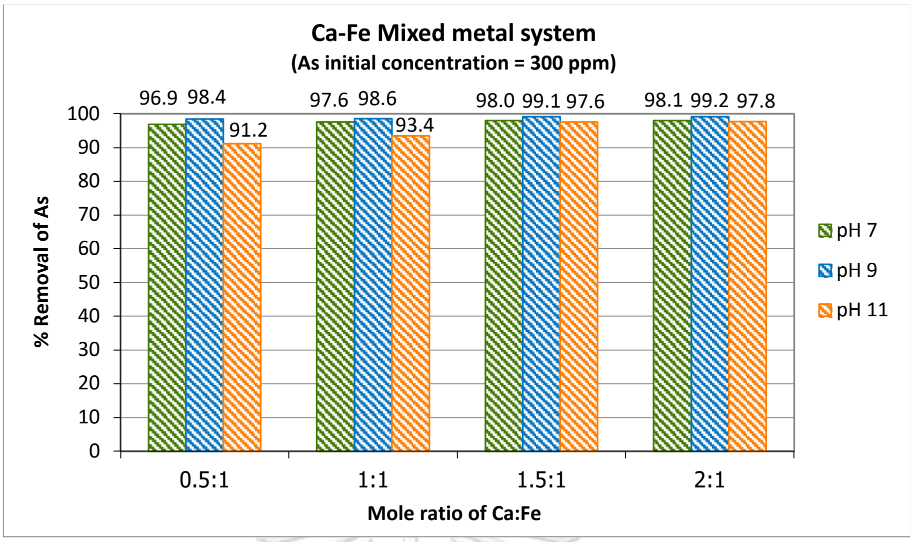

Figure 21. Arsenic removal (%) as a function of mole ratio of Ca: Fe at various pH

This results from Figure 21 were obtained by varying the pH solution (7,9 and 11) and mole ratio of Ca: Fe (0.5:1, 1:1, 1.5:1 and 2:1) by using 2.5:1 of Fe: As mole ratio, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using CaFe mixed metal system. The results showed that the removal efficiency of arsenic remain constant as decreasing of Ca: Fe mole ratio from 2:1 to 0.5:1, at pH7 and 9. Conversely, the arsenic removal efficiency decreased when decreasing of Ca: Fe mole ratio from 2:1 to 0.5:1, at pH11. Moreover, the removal efficiency of arsenic not significantly changed or effected by changing the pH solution at pH7 and 9. But the arsenic removal efficiency decreased at pH11 by using the comparable dosage values of mixed metal.

This could be described by the species distribution of As(III) and As(V) at pH7-11, the neutral form of arsenite (H_3AsO_3) or the deprotonated forms of arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$) at pH7, the neutral and deprotonated forms of arsenite (H_3AsO_3, $H_2AsO_3^-$) or the deprotonated form of arsenate ($HAsO_4^{2-}$) at pH9 present in the solution which favored to coprecipitate with CaFe mixed metal hydroxides. Moreover, the deprotonated or anionic form of arsenite ($H_2AsO_3^-$) at pH9, and the deprotonated forms of arsenate ($H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) at pH7, 9 and 11, can be also precipitated with the ionized form of calcium (Ca^{2+}, $Ca(OH)^+$). On the other hand, when the pH of the solution increased to pH11, the removal efficiency of arsenic decreased via using 1:1 or 0.5:1 mole ratio of Ca: Fe, probably due to the competition between negatively charged of arsenic species and hydroxide ions in coprecipitation process, or the electrostatic repulsion between anionic species of arsenic and negatively charged on metal hydroxides surface, which resulting to the lower arsenic removal efficiency compared with pH7 and 9. Whereas the mole ratio of CaFe at 2:1 and 1.5:1 not significantly effect by pH solution probably due to the increasing of calcium, which resulting to more precipitation or coprecipitation process between negatively charged of arsenic and ionized form of calcium (Ca^{2+}, $Ca(OH)^{+}$).

Table 4.2 Arsenic removal efficiency using mixed metal system at various pH and M^{2+}: M^{3+} mole ratio (Emulated industrial chemicals)

As solution (300 mg/L)			%Removal (M^{2+}: M^{3+} ratio)			
	System	**pH**	**0.5: 1**	**1: 1**	**1.5: 1**	**2: 1**
As(III)+ As(V)	**MgFe**	**7**	97.4 ± 0.1	98.1 ± 0.1	98.1 ± 0.3	98.3 ± 0.5
		9	98.5 ± 0.3	98.2 ± 0.3	98.8 ± 0.0	98.9 ± 0.0
		11	79.2 ± 0.2	84.6 ± 0.5	90.8 ± 0.4	92.4 ± 0.1
	CaFe	**7**	96.9 ± 0.3	97.6 ± 0.2	98.0 ± 0.3	98.1 ± 0.1
		9	98.4 ± 0.1	98.6 ± 0.1	99.1 ± 0.1	99.2 ± 0.0
		11	91.2 ± 0.2	93.4 ± 0.5	97.6 ± 0.1	97.8 ± 0.2

In the previous study, which studied about the investigation of M^{2+}: M^{3+} mole ratio of mixed metal (MgFe and CaFe), and pH of the solution to find out the optimal amount for maximum arsenic removal efficiency. The results from the emulated industrial chemical part showed that the removal efficiency of arsenic remained constant as decreasing of M^{2+}: M^{3+} mole ratio from 2:1 to 0.5:1, at pH7 and 9 for both MgFe and CaFe mixed metal systems. Conversely, the arsenic removal efficiency dramatically decreased when decreasing of M^{2+}: M^{3+} mole ratio at pH11, which is the lowest arsenic removal efficiency compared with pH7 and 9, at comparable dosage values of mixed metal, as shown in Table 4.2.

Therefore, the further investigation of arsenic removal which using 0.5:1 mole ratio of M^{2+}: M^{3+} mixed metal was selected, to investigate the mole ratio of mixed metal and arsenic

($M^{2+}M^{3+}$: As) at 1.25:1, 1.5:1, 2:1 and 2.5:1 for both MgFe and CaFe mixed metal systems in the next following part.

4.2.2.2 Effect of pH and $M^{2+}M^{3+}$: As mole ratio

4.2.2.2.1 MgFe mixed metal system

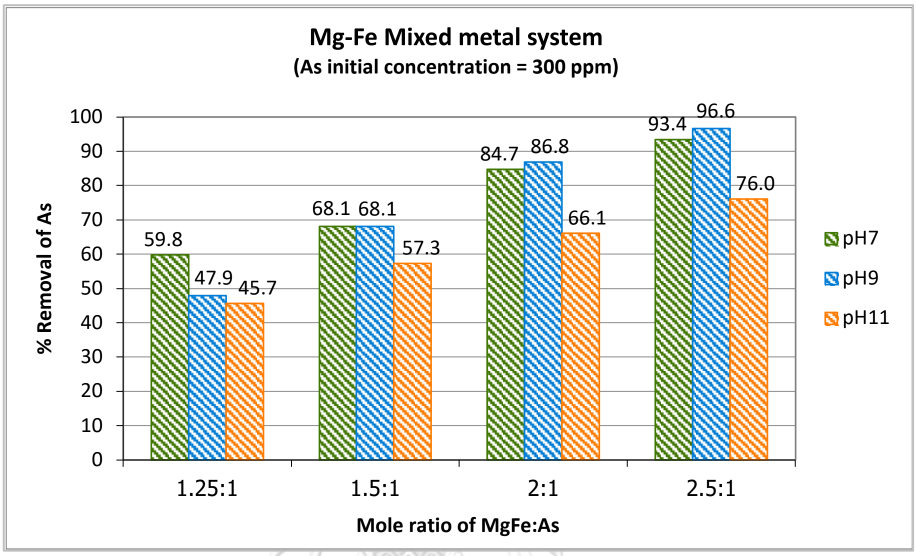

Figure 22. Arsenic removal (%) as a function of mole ratio of MgFe: As at various pH

This results from Figure 22 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of MgFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1), to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system with 0.5:1 of Mg: Fe mole ratio. The results showed that the removal efficiency of arsenic increased with increasing of MgFe: As mole ratio from 1.25: 1 to 2.5: 1, at pH7, 9 and 11. Moreover, the arsenic removal efficiency by using MgFe mixed metal also effected by changing the pH solution. Arsenic, (As(III)+ As(V)) was the most effectively removed at pH9 via using 2.5:1 of MgFe: As mole ratio, while the removal efficiency slightly decreased at pH7 and dramatically decreased at pH11 by using the comparable dosage values of mixed metal system.

4.2.2.2.2 CaFe mixed metal system

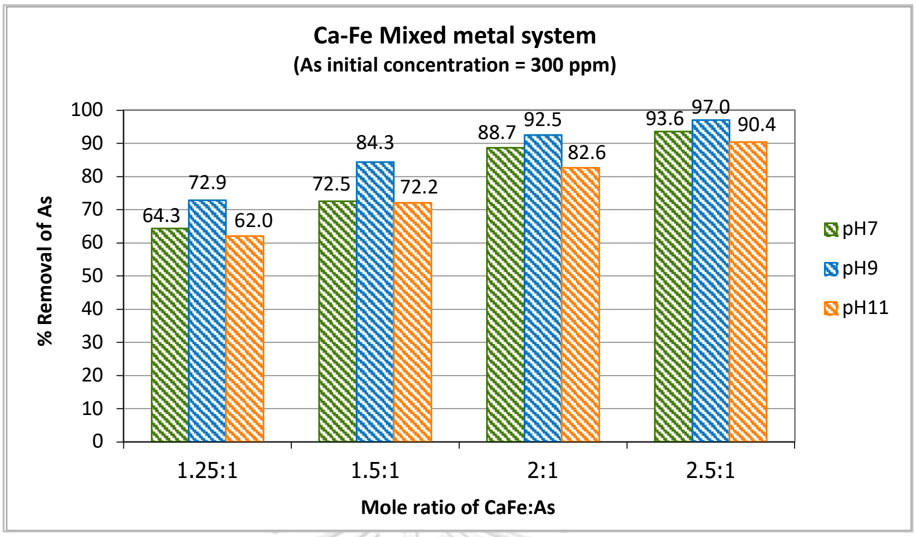

Figure 23. Arsenic removal (%) as a function of mole ratio of CaFe: As at various pH

This results from Figure 23 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of CaFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1), to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using CaFe mixed metal system with 0.5:1 of Ca: Fe mole ratio. The results showed that the removal efficiency of arsenic increased with increasing of CaFe: As mole ratio from 1.25:1 to 2.5:1, at pH7,9 and 11. Moreover, the arsenic removal efficiency by using CaFe mixed metal also affected by changing the pH solution. Arsenic, (As(III)+As(V)) was the most effectively removed at pH9 via using 2.5:1 of CaFe: As mole ratio, while the removal efficiency slightly decreased at pH7 and significantly decreased at pH11, by using the comparable dosage values of mixed metal system.

Table 4.3 Arsenic removal efficiency using mixed metal system at various pH and $M^{2+}M^{3+}$: As mole ratio

As solution (300 mg/L)			**%Removal ($M^{2+}M^{3+}$: As ratio)**			
	System	**pH**	**1.25: 1**	**1.5: 1**	**2: 1**	**2.5: 1**
As(III) + As(V)	**MgFe**	**7**	59.8 ± 2.6	68.1 ± 0.9	84.7 ± 2.7	93.4 ± 0.9
		9	47.9 ± 0.7	68.1 ± 0.6	86.8 ± 0.7	96.6 ± 0.5
		11	45.7 ± 1.9	57.3 ± 2.9	66.1 ± 0.2	76.0 ± 3.0
	CaFe	**7**	64.3 ± 1.2	72.5 ± 1.7	88.7 ± 1.8	93.6 ± 2.2
		9	72.5 ± 0.5	84.5 ± 1.3	92.5 ± 0.2	97.0 ± 0.3
		11	62.0 ± 0.7	72.2 ± 2.0	82.6 ± 1.8	90.4 ± 1.8

For the investigation of $M^{2+}M^{3+}$: As mole ratio as shown in the previous subsections in emulated industrial chemical part, which are summarized in Table 4.3. The results showed that the arsenic removal efficiency was the most effectively at pH9 via using 2.5:1 of MgFe: As and CaFe: As mole ratio, while the removal efficiency slightly decreased at pH7 and dramatically decreased at pH11. Moreover, the arsenic removal efficiency slightly decreased when decreasing of $M^{2+}M^{3+}$: As mole ratio. And the results obviously showed that the arsenic removal efficiency of MgFe mixed metal system was a bit lower than CaFe mixed metal system while decreasing of $M^{2+}M^{3+}$: As mole ratio at the comparable dosage values of mixed metal, probably due to the competition of hydroxide ions present in the solution which favored to form metal hydroxides have more effect on MgFe than CaFe mixed metal system, due to the fact that $Mg(OH)_2$ has more solubility product constant value (k_{sp}) than $Ca(OH)_2$.

Therefore, several operating parameters which possibly affect to the metal hydroxides formation and result in the arsenic removal performance by using MgFe mixed metal system, including step of pH adjustment (continuous, metal pre-added, acid/base pre-added), retention time (0, 5, 15, 30 and 60 minutes), and speed of stirring (0-800 rpm) were studied and investigated in the following subsections.

4.2.2.3 Investigation of parameters for MgFe mixed metal system

4.2.2.3.1 Step of pH adjustment

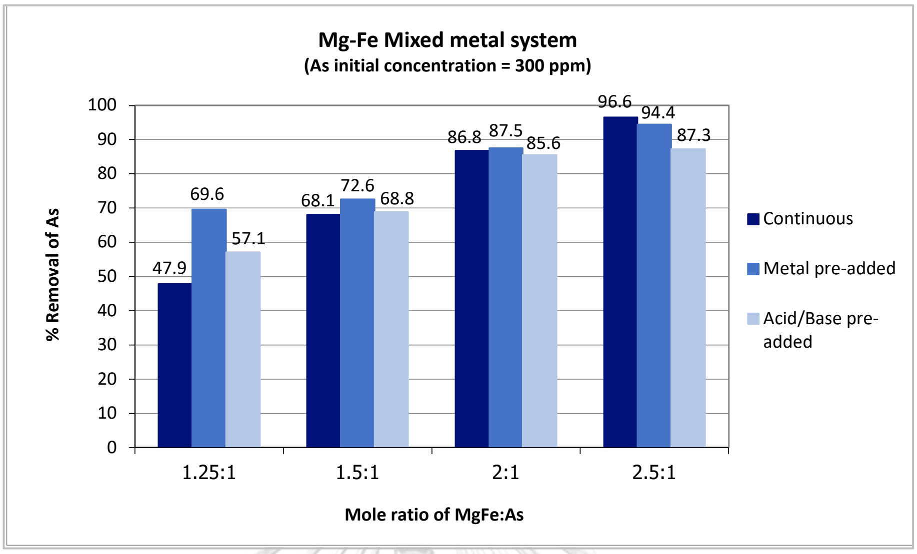

Figure 24. Arsenic removal (%) as a function of mole ratio of MgFe: As at various step of pH adjustment

This results from Figure 24 were obtained by varying the step of pH adjustment (continuous, metal pre-added, acid/base pre-added) and mole ratio of MgFe: As (1.25:1, 1.5:1, 2: 1 and 2.5:1) at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system. The results showed that the removal efficiency significantly effect by the step of pH adjustment. Arsenic, (As(III)+As(V)) was the most effectively removed at lower than 2.5:1 of MgFe: As mole ratio via using metal pre-added as a step of pH adjustment, compared with continuous and acid/base pre-added.

This could be described by the species distribution of As(III) and As(V), the neutral and deprotonated forms of arsenite (H_3AsO_3 $H_2AsO_3^-$) or the deprotonated form of arsenate ($HAsO_4^{2-}$) at pH9 present in the solution which favored to coprecipitate with MgFe mixed metal hydroxides. However, the step of pH adjustment is one of parameters that affecting to the arsenic removal efficiency, probably due to the different competition between negatively charged of arsenic and hydroxide ions in coprecipitation process at different addition sequence of hydroxide ions (continuous, metal pre-added, acid/base pre-added). Therefore, the arsenic removal efficiency by using metal pre-added as a step of pH adjustment was an optimal operating parameter which resulting to the most effective for arsenic removal percentage, possibly due to the excess of mixed metal salts in arsenic solution and the lower competition between anionic species of negatively charged of arsenic and hydroxide ions to coprecipitate, compared with continuous and acid/base pre-added as a step of pH adjustment.

4.2.2.3.2. Retention time

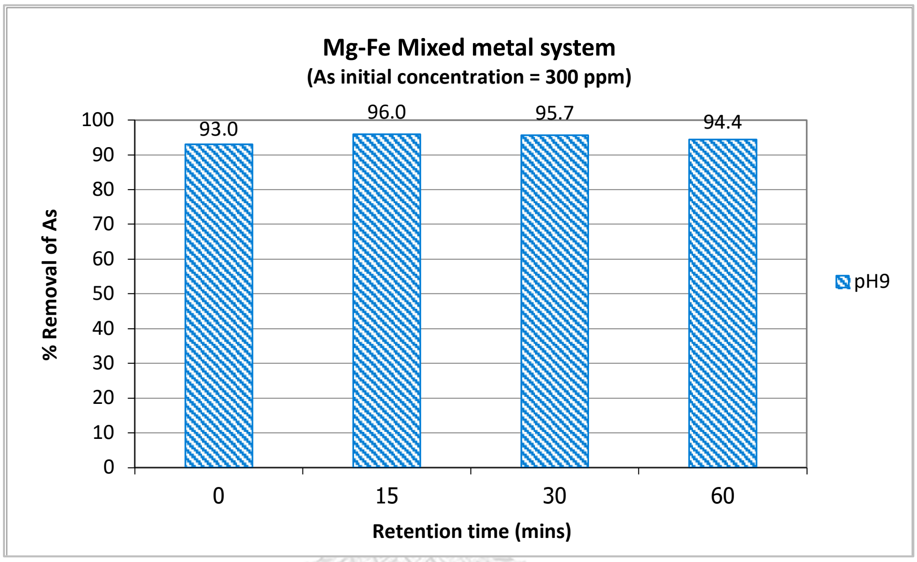

Figure 25. Arsenic removal (%) as a function of various retention time (minute) at pH9

This results from Figure 25 were obtained by varying the retention time or mixing time (0, 15, 30 and 60 minutes) via using 2.5: 1 of MgFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system. The results showed that the removal efficiency of arsenic slightly increased when increasing the retention time from 0 to 15 minutes, then the removal efficiency slightly decreased for further increasing of retention time from 15 to 60 minutes. Therefore, it can be concluded that arsenic was the most effectively removed at 15 minutes of retention time.

This could be described by the species distribution of As(III) and As(V), the neutral and deprotonated form of arsenite (H_3AsO_3, $H_2AsO_3^-$) or the deprotonated form of arsenate ($HAsO_4^{2-}$) at pH9 present in the solution which favored to coprecipitate with MgFe mixed metal hydroxides. Nevertheless, the retention time or mixing time is one of the parameters that also play an important role of flocs formation in coprecipitation process, due to the fact of the collisions between metal salts (coagulants), and arsenic or colloidal suspension are not efficient to coprecipitate if mixing time is too short. Therefore, it was crucial to consider and determine the optimal retention time in order to minimize the energy and time consumption as possible, while the effective arsenic removal in treatment process can be obtained.

Thereby, the further investigation in the next following subsection which investigated about the speed of stirring for providing the lowest of energy and time consumption, via using 0 minute for retention time.

4.2.2.3.3 Speed of stirring

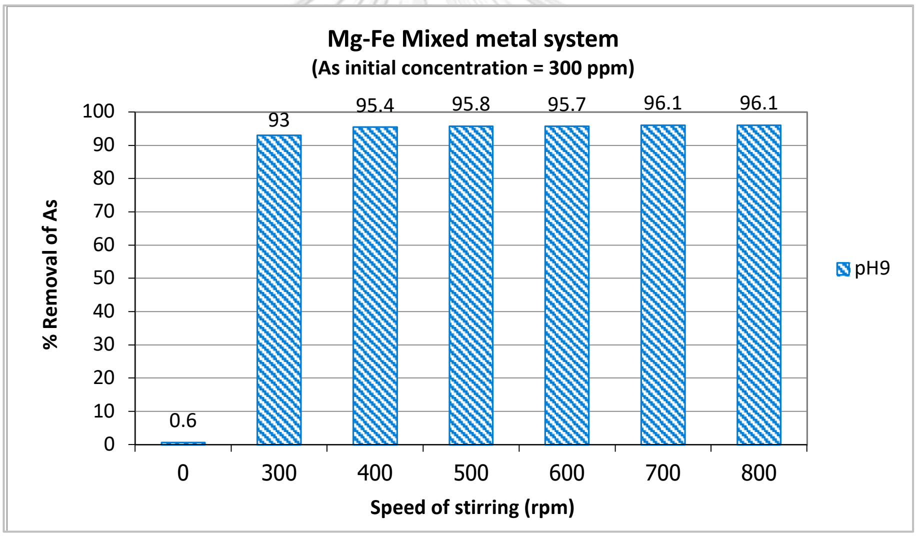

Figure 26. Arsenic removal (%) as a function of various speed of stirring (rpm) at pH9

This results from Figure 26 were obtained by varying the speed of stirring (0-800 rpm) via using 2.5:1 of MgFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system. The results showed that the removal efficiency of arsenic dramatically increased when increasing speed of stirring from 0 to 300 rpm and it slightly increased when increasing speed of stirring from 300 to 400 rpm, then the removal efficiency remain constant for the further increasing from 400 to 800 rpm. Therefore, it can be concluded that arsenic was the most effectively removed at 400 rpm for speed of stirring via using 0 minute for retention time, to provide sufficient collision between metal salts (coagulants), and arsenic for coprecipitation process.

Table 4.4 Optimal operating condition of mixed metal system for arsenic removal process

As solution (300 mg/L)			
As(III)+As(V)	**System**	**Factor**	**Optimal condition**
	MgFe	**Step of pH adjustment**	Metal pre-added
		Retention time (min)	0
		Speed of stirring (rpm)	400

For the previous study, several operating parameters for arsenic removal via using MgFe mixed metal system were investigated, including step of pH adjustment, retention time, and speed of stirring. The results showed that the most effective operating parameters for arsenic removal with the lowest of energy and time consumption, was metal pre-added as a step of pH adjustment, 0 minute for retention time and 400 rpm for speed of stirring, as summarized and shown in Table 4.4.

Therefore, these effective operating parameters were selected and used to perform for removing of arsenic by using 1.25:1, 1.5:1, 2:1 and 2.5:1 mole ratio of $M^{2+}M^{3+}$: As, for both MgFe and CaFe mixed metal systems at pH7, 9 and 11, as shown the results and discussion in the next following subsections.

4.2.3 Removal efficiency by mixed metal system under optimal condition

4.2.3.1 MgFe mixed metal system

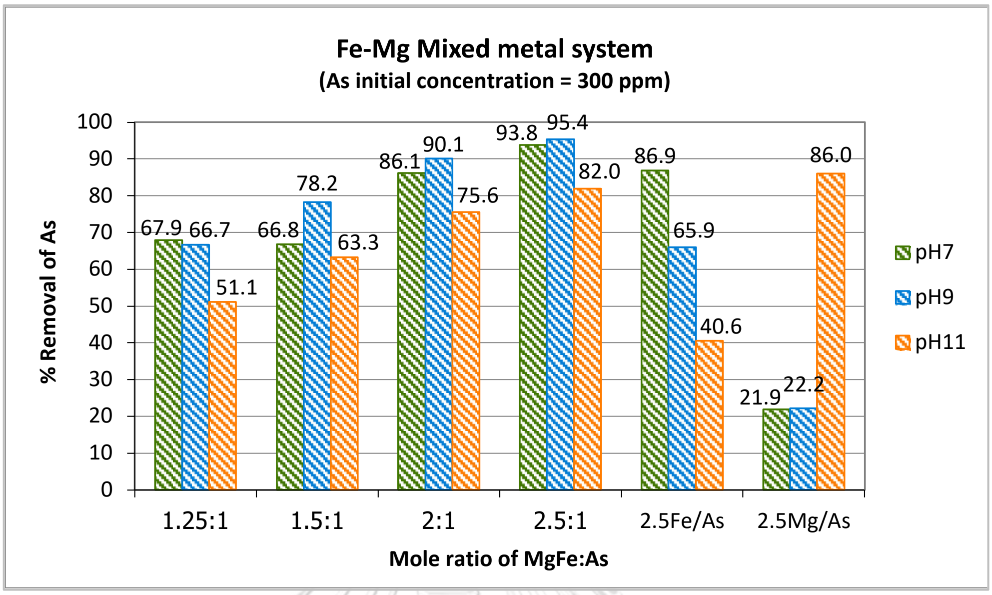

Figure 27. Arsenic removal (%) as a function of mole ratio of MgFe: As at various pH

The results from Figure 27 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of MgFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1) under optimal operating parameters (metal pre-added as a step of pH adjustment, 0 minute for retention time with 400 rpm for speed of stirring) which provided the lowest energy and time consumption as possible, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using MgFe mixed metal system. The results showed that the removal efficiency of arsenic increased with increasing of MgFe: As mole ratio from 1.25:1 to 2.5:1, at pH7, 9 and 11. Moreover, the arsenic removal efficiency by using MgFe mixed metal also effected by changing the pH solution. The efficiency of arsenic removal was approximately 67.9-93.8%, 66.7-95.4%, and 51.1-82.0%, by using MgFe mixed metal at pH7, 9 and 11, consecutively. As the results of the using of MgFe mixed metal to coprecipitate with arsenic for arsenic removal process, arsenic (As(III)+As(V)) was the most effectively removed at pH9 via using 2.5:1 of MgFe: As mole ratio, while the removal efficiency slightly decreased at pH7, and dramatically decreased at pH11 at the comparable dosage values of MgFe mixed metal system.

This could be described by the species distribution of arsenic at pH9 (H_3AsO_3, $H_2AsO_3^-$, $HAsO_4^{2-}$) present in the solution which are more favorable coprecipitated with MgFe mixed metal hydroxides than the arsenic species at pH7 (H_3AsO_3, $H_2AsO_4^-$, $HAsO_4^{2-}$) and pH11 ($H_2AsO_3^-$, $HAsO_3^{2-}$, $HAsO_4^{2-}$, AsO_4^{3-}). Moreover, the arsenic species were not only removed by coprecipitation process, but they were also removed by precipitation with the ionized form of magnesium at pH9. However, the removal efficiency of arsenic decreased when increasing the pH solution to pH11, probably due to the competition between anionic of arsenic species and hydroxide ions or negatively charged on metal hydroxide form.

4.2.3.2 CaFe mixed metal system

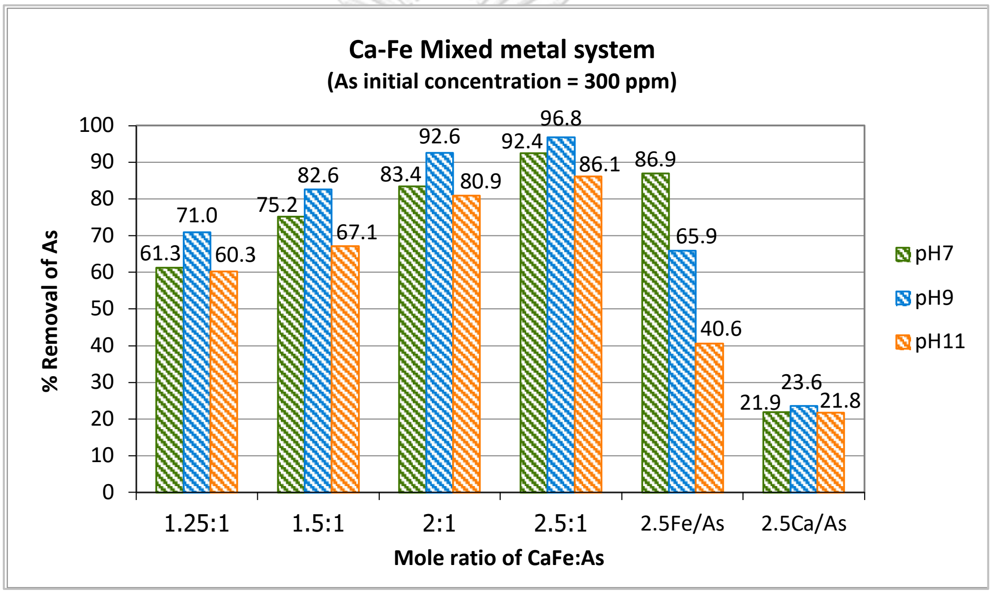

Figure 28. Arsenic removal (%) as a function of mole ratio of CaFe: As at various pH

The results from Figure 28 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of CaFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1) under optimal operating parameters (metal pre-added as a step of pH adjustment, 0 minute for retention time with 400 rpm for speed of stirring) which provided the lowest energy and time consumption as possible, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using CaFe mixed metal system. The results showed that the removal efficiency of arsenic increased with increasing of CaFe: As mole ratio from 1.25:1 to 2.5:1, at pH7, 9 and 11. Moreover, the arsenic removal efficiency by using CaFe mixed metal also effected by changing the pH solution. The efficiency of arsenic removal was approximately 61.3-92.4%, 71.0-96.8%, and 60.3-86.1%, by using CaFe mixed metal system at pH7, 9 and 11, consecutively. As the results of the using of CaFe mixed metal to coprecipitate with arsenic for arsenic removal process, arsenic (As(III)+As(V)) was the most effectively removed at pH9 via using 2.5:1 of CaFe: As mole ratio, while the removal efficiency slightly decreased at pH7, and dramatically decreased at pH11 at the comparable dosage values of CaFe mixed metal system.

This could be described by the species distribution of arsenic at pH9 (H_3AsO_3, $H_2AsO_3^-$, $HAsO_4^{2-}$) present in the solution which are more favorable coprecipitated with CaFe mixed metal hydroxides than the arsenic species at pH7 (H_3AsO_3, $H_2AsO_4^-$, $HAsO_4^{2-}$) and pH11 ($H_2AsO_3^-$, $HAsO_3^{2-}$, $HAsO_4^{2-}$, AsO_4^{3-}). Moreover, the arsenic species were not only removed by coprecipitation process, but they were also removed by precipitation with the ionized form of calcium at pH9 and 11. Nevertheless, the removal efficiency of arsenic decreased when increasing the pH solution to pH11, probably due to the competition between anionic of arsenic species, and hydroxide ions or negatively charged on metal hydroxides form.

Table 4.5 Optimal condition of mixed metal system for the most effective arsenic removal by coprecipitation process

As solution (300 mg/L)			
	System	Factor	Optimal condition
As(III)+As(V)	MgFe or CaFe	pH	9
		M^{2+}: M^{3+}	0.5:1
		$M^{2+}M^{3+}$: As	2.5:1
		Step of pH adjustment	Metal pre-added
		Retention time (min)	0
		Speed of stirring (rpm)	400

Coprecipitation process of arsenic removal by using mixed metal systems (MgFe, CaFe, MgAl and CaAl) as coagulants, was investigated and reported the results as mentioned above. All of the results suggested that the arsenic removal efficiency via mixed metal systems which using ferric chloride ($FeCl_3$) as trivalent metal salts (MgFe and CaFe) to precipitate arsenic, was more effective than using aluminum chloride ($AlCl_3$) as trivalent metal salts (MgAl and CaAl). Furthermore, the efficacy of coprecipitation method by using mixed metal as coagulants is influenced by various operating parameters, including pH of the solution, M^{2+}: M^{3+} mole ratio, $M^{2+}M^{3+}$: As mole ratio, step of pH adjustment, retention time, and speed of stirring. Then, the optimal condition for effective removing of arsenic was used to perform for arsenic removal efficiency for both MgFe and CaFe mixed metal systems, as shown in the previous subsections which showed the most effective of arsenic removal efficiency was approximately 95.4% and 96.8%, via using 2.5MgFe/As and 2.5CaFe/As at pH9, respectively. Furthermore, for comparing the arsenic removal efficiency by coprecipitation method, using $2.5M^{2+}M^{3+}$/As mixed metal system at pH9, to 2.5Fe/As, 2.5Mg/As, and 2.5Ca/As single component systems, the results showed that the arsenic removal efficiency for mixed metal system was greater than the single component system at comparable optimal dosage values for both MgFe and CaFe mixed metal systems.

4.2.4 Characterization of the arsenic coprecipitated MgFe mixed metal

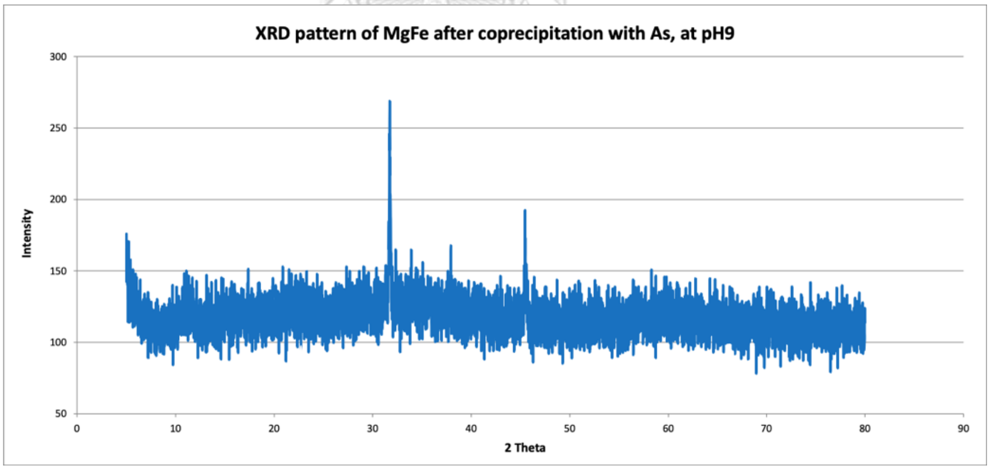

Figure 29. XRD pattern of arsenic coprecipitated MgFe mixed metal, at pH9

The result from Figure 29, showed the XRD pattern of arsenic coprecipitated with MgFe mixed metal system at pH9, which is the most effective condition for arsenic removal efficiency by coprecipitation method. The XRD result showed that the intensities of XRD pattern of arsenic coprecipitates was quite low, which could be indicated that coprecipitate formed of arsenic and mixed metal hydroxides form were poorly crystalline under this effective condition. Furthermore, the coprecipitated of mixed metal hydroxides was probably amorphous, and its XRD diffraction bands which can be mixed metal oxides, ferric arsenite etc., may be obscured or not clearly showed by those of poorly crystalline substances [58, 59].

However, the used of inorganic metal salts or chemical methods, can cause the toxicity to the living organism from sludge production. Alternatively, the use of biopolymers as flocculants or coagulant aids also has useful properties over inorganic metal salts such as large flocs formation and high settling properties. Hence, the coprecipitation techniques which use mixed metal salts as coagulants combine with biopolymers (alginate, chitosan) as flocculants, were also studied and evaluated in the next following sections.

4.3 Optimization of mixed metal and biopolymer systems for arsenic removal

For improving the arsenic removal, biodegradability and low toxicity from sludge production, thereby the coprecipitation techniques which use the synergistic effect of mixed metal salts as coagulants combine with biopolymers as flocculants were studied for finding the optimum amount and condition for effective arsenic removal treatment process. Arsenic is easily coprecipitated with coagulants (inorganic mixed metal salts), then the flocculants (biopolymers) is added to form the larger particles or allowed to settle by themselves. Based on biopolymers, alginate (ALG, $pK_a = 3.5$), and chitosan (CTS, $pK_a = 6.2$) are interesting because of their unique properties.

In this study, a ratio of $1.25M^{2+}M^{3+}$/ As which is the lowest arsenic removal efficiency (see Figures 27-28), was selected to perform the experiments because this condition could allow to observed an improvement of the arsenic removal efficiency with the aid of biopolymers. The synergistic effect of mixed metal (MgFe and CaFe) combine with biopolymer (alginate or chitosan) systems were investigated by several parameters, including biopolymers concentration (%w/v), retention time (minute), and pH of the solution (7, 9 and 11), by using 300 mg/L as an initial concentration of simulated wastewater, 4As(III): 1As(V) solution.

4.3.1 Effect of biopolymer concentration and retention time

4.3.1.1 Combination of mixed metal and alginate (ALG) system

4.3.1.1.1 MgFe mixed metal with ALG system

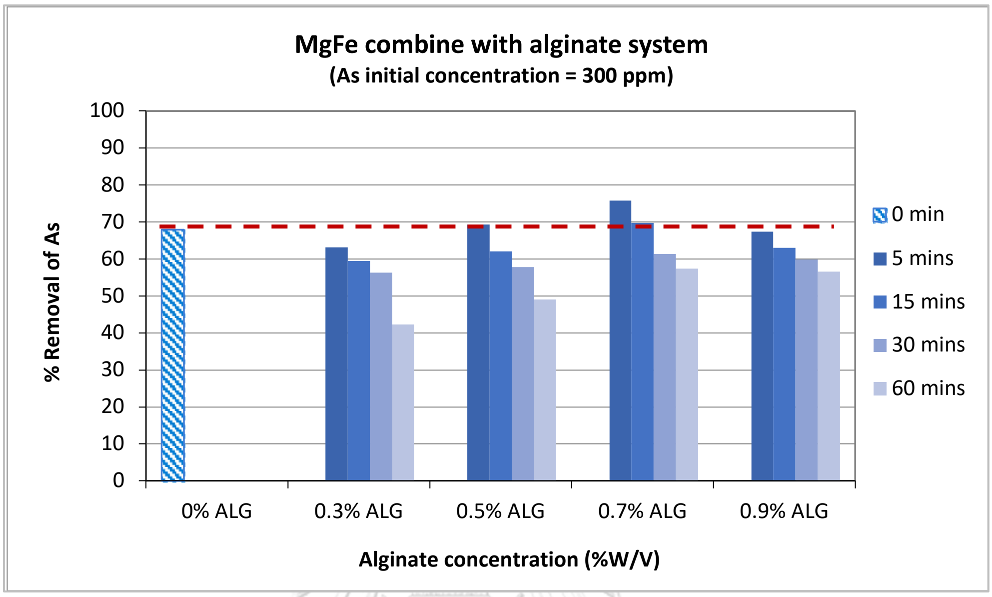

Figure 30. Arsenic removal (%) as a function of alginate concentration (%w/v) combine with 1.25MgFe/As

Table 4.6 Comparison of arsenic removal efficiency using 1.25MgFe/As, and 1.25MgFe/As combine with alginate at various concentration and retention time

Retention time (minute)	%Removal (1.25MgFe/As + ALG (%w/v))				
	0% ALG	0.3% ALG	0.5% ALG	0.7% ALG	0.9% ALG
0	66.7 ± 0.2	-	-	-	-
5	-	63.1 ± 0.3	69.3 ± 0.8	75.8 ± 1.0	67.4 ± 1.1
15	-	59.4 ± 1.8	62.0 ± 0.5	69.7 ± 1.7	63.0 ± 0.8
30	-	56.3 ± 0.7	57.8 ± 1.4	61.3 ± 0.9	59.9 ± 1.0
60	-	42.3 ± 0.5	49.0 ± 1.4	57.4 ± 0.5	56.6 ± 1.0

The results from Figure 30 and Table 4.6, were obtained by varying the retention time (5, 15, 30 and 60 minutes) and alginate concentration (%w/v) by using 1.25:1 of MgFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of MgFe mixed metal and alginate (ALG) system. The results showed that the removal efficiency of arsenic increased when increasing alginate concentration from 0.3% to 0.7% at 5, 15, 30 and 60 minutes for retention time. Conversely, the arsenic removal efficiency decreased when increasing the alginate concentration from 0.7% to 0.9% at 5, 15, 30 and 60 minutes for retention time. Moreover, the arsenic removal efficiency by using the combination of MgFe mixed metal and alginate not only effected by the alginate concentration, but it also effected by varying the retention time. Arsenic (As(III)+As(V)) was the most effectively removed at 5 minutes for retention time, via using 1.25MgFe/As combine with 0.7% of alginate, while the removal efficiency decreased when increasing retention time from 5 to 60 minutes at the comparable dosage values of mixed metal combine with alginate system.

This could be described by the negatively charged of arsenic, and the carboxylic functional groups (-COOH) of alginate which is easily deprotonated at higher pH to form carboxylate ($-COO^-$) at pH9, resulting in the electrostatic repulsions in solution. Therefore, when the alginate concentration increased to 0.9%, the possesses excess negatively charged of alginate in solution results in flocs stabilization with the decreasing of arsenic removal efficiency. However, the nature of alginate favors removal of arsenic by bridging mechanism. Thus, the combined use of MgFe mixed metal and 0.7% of alginate has synergistic effects according to the enhanced of arsenic removal, which is approximately 8% greater than only 1.25MgFe/As mixed metal system. Furthermore, the retention time is another parameter that affecting to the arsenic removal performance, probably due to the longer mixing time will lead to an increase in flocculate chains breakage and limiting the size of flocs formed which resulting to restabilizing mechanism.

4.3.1.1.2 CaFe mixed metal with ALG system

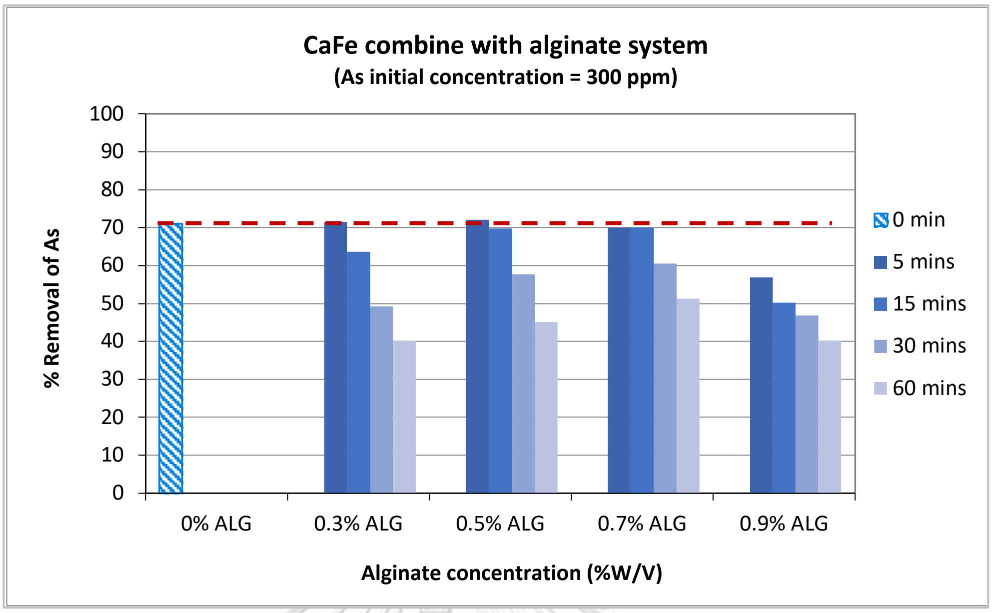

Figure 31. Arsenic removal (%) as a function of alginate concentration (%w/v) combine with 1.25CaFe/As

Table 4.7 Comparison of arsenic removal efficiency using 1.25CaFe/As, and 1.25CaFe/As combine with alginate at various concentration and retention time

Retention time (minute)	%Removal (1.25CaFe/As + % ALG (%w/v))				
	0% ALG	0.3% ALG	0.5% ALG	0.7% ALG	0.9% ALG
0	71.0 ± 0.6	-	-	-	-
5	-	71.5 ± 1.2	72.0 ± 0.4	70.1 ± 1.4	56.9 ± 1.0
15	-	63.6 ± 1.1	69.8 ± 0.4	70.0 ± 1.4	50.2 ± 1.6
30	-	49.2 ± 0.7	57.7 ± 1.2	60.5 ± 2.2	46.9 ± 1.1
60	-	40.2 ± 1.4	45.1 ± 1.6	51.3 ± 2.3	40.1 ± 0.4

The results from Figure 31 and Table 4.7, were obtained by varying the retention time (5, 15, 30 and 60 minutes) and alginate concentration (%w/v) by using 1.25:1 of CaFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of CaFe mixed metal and alginate (ALG) system. The results showed that the removal efficiency of arsenic increased when increasing of alginate concentration from 0.3% to 0.7%, especially at 15, 30 and 60 minutes for retention time. Conversely, the arsenic removal efficiency decreased when increasing the alginate concentration from 0.7% to 0.9% at 5, 15, 30 and 60 minutes for retention time. Moreover, the arsenic removal efficiency by using the combination of CaFe mixed metal and alginate not only effected by the alginate concentration, but it also effected by varying the retention time. Arsenic (As(III)+As(V)) trends to has the most effective of arsenic removal at 5 minutes for retention time, via using 1.25 CaFe/As combine with 0.7% of alginate, while the removal efficiency decreased when increasing the retention time from 5 to 60 minutes at the comparable dosage values of mixed metal combine with alginate system.

This could be described by the negatively charged of arsenic and the carboxylic functional groups (-COOH) of alginate which is easily deprotonated at higher pH to form carboxylate ($-COO^-$) at pH9, resulting in the electrostatic repulsions in solution. Therefore, when the alginate concentration increased to 0.9%, the possesses excess negatively charged of alginate in solution results in flocs stabilization with the decreasing of arsenic removal efficiency. Furthermore, the retention time is another parameter that affecting to the arsenic removal performance, probably due to longer mixing time will lead to an increase in flocculate chains breakage and limiting the size of flocs formed which resulting to restabilizing mechanism. However, the nature of alginate favors removal of arsenic by bridging mechanism. Thus, the combined use of CaFe mixed metal with alginate did not facilitate the removal of arsenic.

4.3.1.2 Combination of mixed metal and chitosan (CTS) system

4.3.1.2.1 MgFe mixed metal with CTS system

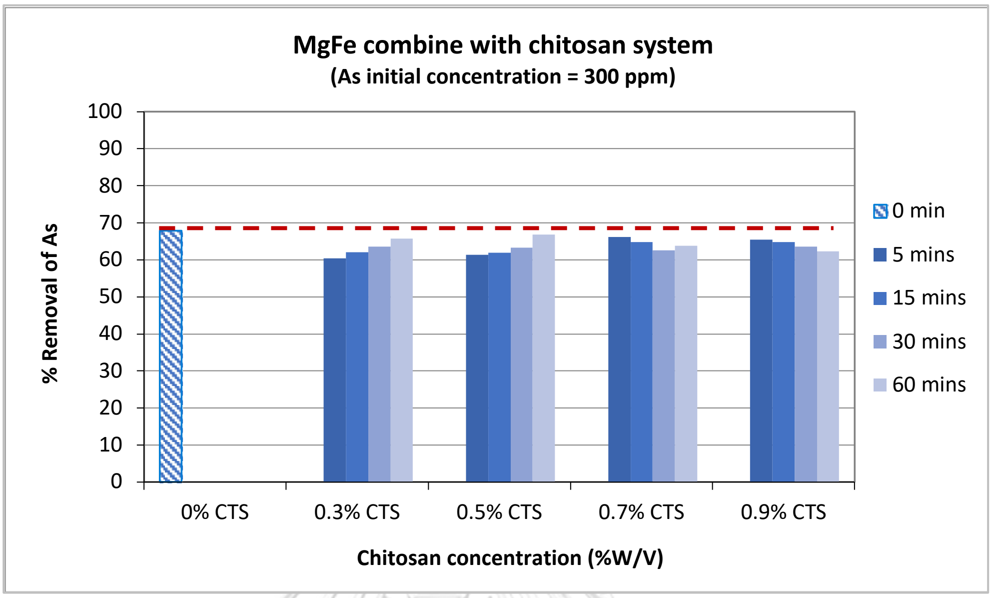

Figure 32. Arsenic removal (%) as a function of chitosan concentration (%w/v) combine with 1.25MgFe/As

Table 4.8 Comparison of arsenic removal efficiency using 1.25MgFe/As, and 1.25MgFe/As combine with chitosan at various concentration and retention time

Retention time (minute)	%Removal (1.25MgFe/As + % CTS (%w/v))				
	0% CTS	0.3% CTS	0.5% CTS	0.7% CTS	0.9% CTS
0	66.7 ± 0.2	-	-	-	-
5	-	60.4 ± 0.5	61.4 ± 0.9	66.1 ± 0.3	65.5 ± 0.6
15	-	62.0 ± 0.6	61.9 ± 0.5	64.8 ± 0.8	64.8 ± 0.2
30	-	63.5 ± 0.6	63.3 ± 0.6	62.6 ± 0.4	63.6 ± 0.2
60	-	65.8 ± 1.3	66.9 ± 0.6	63.9 ± 1.2	62.3 ± 0.8

The results from Figure 32 and Table 4.8, were obtained by varying the retention time (5, 15, 30 and 60 minutes) and chitosan concentration (%w/v) by using 1.25:1 of MgFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of MgFe mixed metal and chitosan (CTS) system. The results showed that the removal efficiency of arsenic increased when increasing chitosan concentration, especially from 0.3% to 0.7%, and it remain constant as the further increasing of chitosan concentration from 0.7% to 0.9% at 5 and 15 minutes for retention time. Conversely, the arsenic removal efficiency remained constant and slightly decreased as increasing chitosan concentration from 0.3% to 0.9% at the retention time of 30 and 60 minutes, respectively. Moreover, the arsenic removal efficiency by using the combination of MgFe mixed metal and chitosan not only effected by chitosan concentration, but it also effected by varying the retention time. Arsenic (As(III)+As(V)) was the most effectively removed via using 1.25MgFe/As combine with 0.3% or 0.5% of chitosan, at 60 minutes for retention time, and it decreased when decreasing retention time from 60 to 5 minutes. Conversely, the arsenic removal was the most effectively removed via using 1.25MgFe/As combine with 0.7% or 0.9% of chitosan, at the retention time of 5 minutes, and it also decreased when increasing retention time from 5 to 60 minutes. Nevertheless, the combined use of MgFe mixed metal with chitosan trends to reduce the arsenic removal performance for all of the various retention time and chitosan concentration, compared with only 1.25MgFe/As mixed metal system.

This could be described by the surface functional groups of chitosan, including hydroxyl (-OH) and amine (-NH_2) on their surface which become negatively charged at alkaline condition (pH>7). Therefore, the importantly charge neutralization mechanism which is a key step of chitosan for coagulation or flocculation was not occurred. Moreover, the possesses of net negative charge on chitosan at pH9 could form the electrostatic repulsion between anionic species of arsenic and negatively charged functional groups of chitosan, leading to decrease the arsenic removal efficiency.

4.3.1.2.2 CaFe mixed metal with CTS system

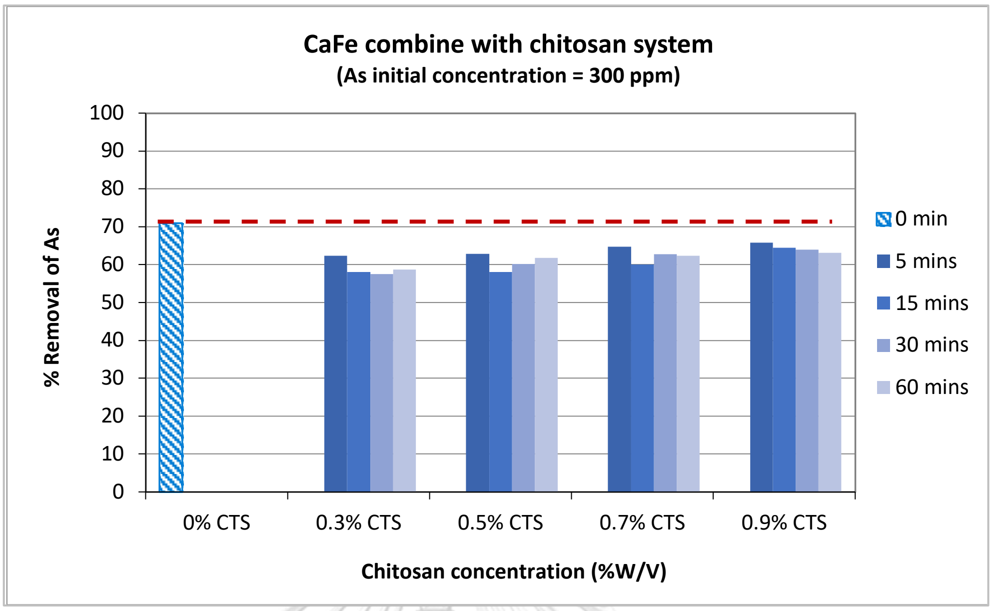

Figure 33. Arsenic removal (%) as a function of chitosan concentration (%w/v) combine with 1.25CaFe/As

Table 4.9 Comparison of arsenic removal efficiency using 1.25CaFe/As, and 1.25CaFe/As combine with chitosan at various concentration and retention time

Retention time (minute)	%Removal (1.25CaFe/As + % CTS (%w/v))				
	0% CTS	0.3% CTS	0.5% CTS	0.7% CTS	0.9% CTS
0	71.0 ± 0.6	-	-	-	-
5	-	62.3 ± 0.3	62.9 ± 1.7	64.8 ± 1.2	65.8 ± 1.1
15	-	58.0 ± 1.0	58.0 ± 1.2	60.0 ± 0.4	64.5 ± 0.9
30	-	57.5 ± 0.6	60.2 ± 0.4	62.8 ± 0.6	63.9 ± 0.7
60	-	58.7 ± 1.3	61.8 ± 1.8	62.4 ± 0.8	63.1 ± 1.0

The results from Figure 33 and Table 4.9, were obtained by varying the retention time (5, 15, 30 and 60 minutes) and chitosan concentration (%w/v) by using 1.25:1 of CaFe: As mole ratio at pH9, to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of CaFe mixed metal and chitosan (CTS) system. The results showed that the removal efficiency of arsenic increased when increasing chitosan concentration from 0.3% to 0.9% at 5, 15, 30 and 60 minutes for retention time. Moreover, the arsenic removal efficiency by using the combination of CaFe mixed metal and chitosan not only effected by chitosan concentration, but it also effected by varying the retention time. Nevertheless, the combined use of CaFe mixed metal with chitosan trends to reduce the arsenic removal performance for all of the various retention time and chitosan concentration, compared with 1.25 CaFe/As mixed metal.

This could be described by the surface functional groups of chitosan, including hydroxyl (-OH) and amine (-NH_2) on their surface which become negatively charged at alkaline condition (pH>7). Therefore, the importantly charge neutralization mechanism which is a key step of chitosan for coagulation or flocculation was not occurred. Moreover, the possesses of net negative charge on chitosan at pH9 could form the electrostatic repulsion between anionic species of arsenic and negatively charged functional groups of chitosan, leading to decrease the arsenic removal efficiency.

Table 4.10 Arsenic removal efficiency by effective combination of mixed metal and biopolymer system, at pH9

As solution (300 ppm)		**%Removal ($M^{2+}M^{3+}$ + % ALG)**	
As(III)+As(V)	**System**	**0% ALG**	**0.7% ALG**
	1.25MgFe	66.7 ± 0.2	75.8 ± 1.0

For the combination of mixed metal (MgFe or CaFe) and biopolymer (alginate or chitosan) as shown in the previous study, which studied about the investigation of biopolymers concentration (0.3, 0.5, 0.7 and 0.9%w/v) and retention time (5, 15, 30 and 60 minutes) to find out the optimal amount and condition for the most effective of arsenic removal process via using mixed metal combine with biopolymer system. The results suggested that alginate has a great potential or the synergistic effect to combined with mixed metal than chitosan system, due to the combination of 1.25MgFe/As and 0.7% of alginate could enhance the removal efficiency compared with only 1.25MgFe/As mixed metal system, as shown in Table 4.10.

Therefore, 0.7%w/v of alginate were performed for the further investigation which investigated about pH solution (7,9 and 11) and mole ratio of $M^{2+}M^{3+}$: As (1.25:1, 1.5:1, 2:1 and 2.5:1) for both MgFe and CaFe mixed metal system, to evaluate the effect of biopolymers due to its pH-dependent forms of charge density, via using the retention time of 5 minutes, as shown in the following subsections.

4.3.2 Effect of biopolymer at various pH and $M^{2+}M^{3+}$: As mole ratio

4.3.2.1 MgFe mixed metal with alginate (ALG) system

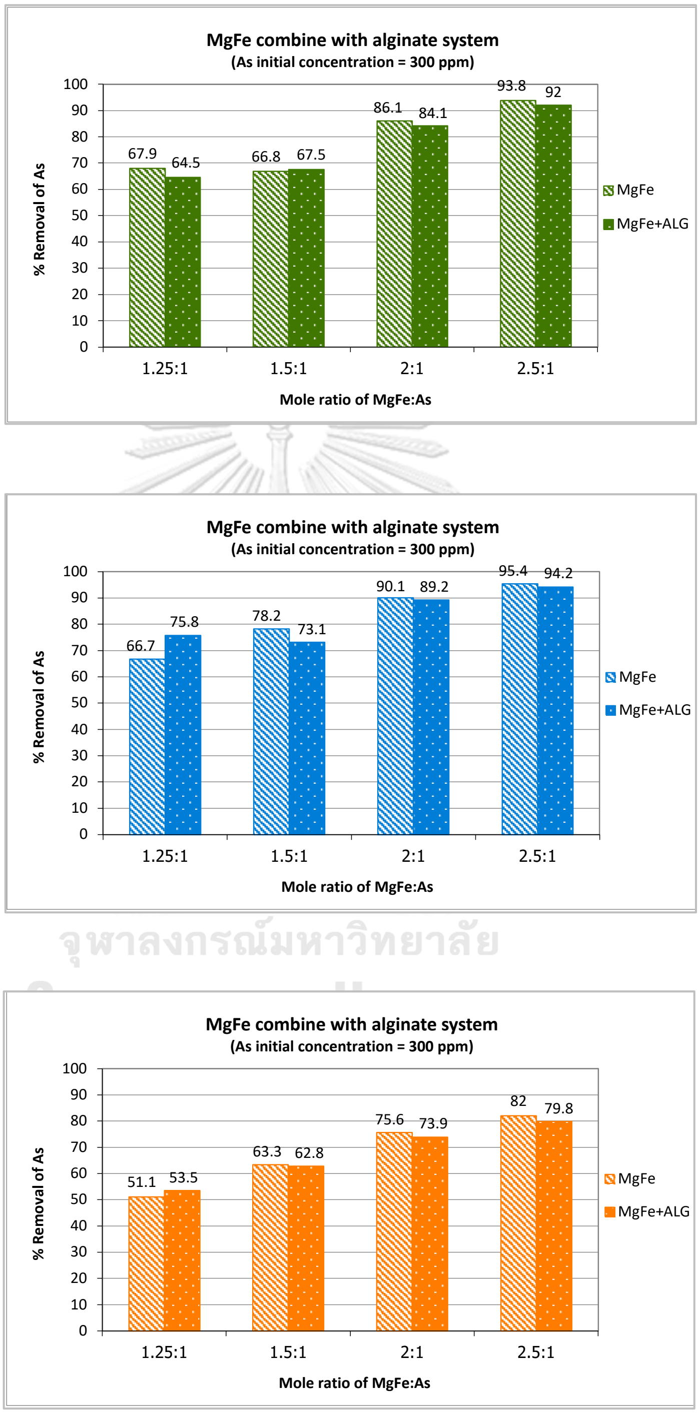

Figure 34. Arsenic removal (%) as a function of mole ratio of MgFe: As, combine with 0.7% ALG at pH7, 9, and 11, respectively.

The results from Figure 34 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of MgFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1), to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of MgFe mixed metal and 0.7%w/v of alginate, at 5 minutes for retention time. The results showed that the removal efficiency of arsenic via using 1.25MgFe/As combine with 0.7% of alginate at pH9 was higher than the system without biopolymers added. Furthermore, the arsenic removal efficiency for the combination of 1.25MgFe/As and 0.7% of alginate system at pH9 was approximately 9% greater than only MgFe mixed metal system at comparable optimal dosage values. Conversely, at other combination conditions of MgFe mixed metal and alginate system, the removal efficiency of arsenic was lower than only MgFe mixed metal system.

This could be described by the species distribution of arsenite (As(III)), arsenate (As(V)), MgFe mixed metal, and pH-dependent forms of charge density on alginate which could be resulted in electrostatic repulsion between anionic species of arsenic and carboxylate ($-COO^-$) functional groups on alginate surface, or the competition between anionic species of arsenic and the negatively charged of carboxylate functional groups on alginate surface which can coprecipitate with the ionized form of magnesium by electrostatic interaction, result in the decreasing of arsenic removal efficiency. However, the nature of alginate could remove arsenic via bridging mechanism varies on their molecular weight.

4.3.2.2 CaFe mixed metal with alginate (ALG) system

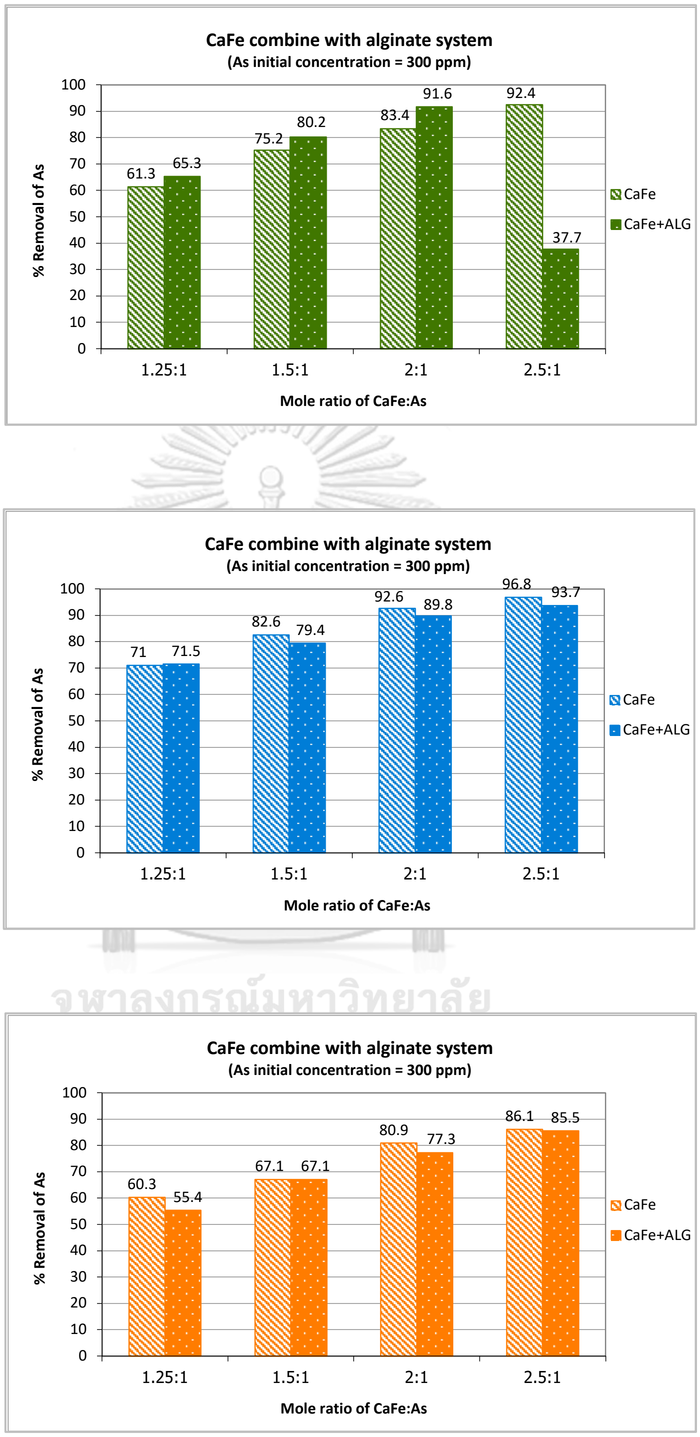

Figure 35. Arsenic removal (%) as a function of mole ratio of CaFe: As, combine with 0.7% ALG at pH7, 9, and 11, respectively.

The results from Figure 35 were obtained by varying the pH solution (7, 9 and 11) and mole ratio of CaFe: As (1.25:1, 1.5:1, 2:1 and 2.5:1), to evaluate the removal efficiency of arsenic from simulated wastewater which containing 300 mg/L of 4As(III): 1As(V) solution by using the combination of CaFe mixed metal and 0.7%w/v of alginate, at 5 minutes for retention time. The results showed that the removal efficiency of arsenic via using 1.25, 1.5 and 2.0 CaFe/As combine with 0.7% of alginate at pH7 was higher than the system without biopolymers added. Furthermore, the arsenic removal efficiency for the combination of 1.25, 1.5 and 2.0 CaFe/As and 0.7% of alginate system at pH7 was approximately 4-8% greater than only CaFe mixed metal system at comparable optimal dosage values. Conversely, at the other combination conditions of CaFe mixed metal and alginate system, the removal efficiency of arsenic was lower than only CaFe mixed metal, especially at 2.5 CaFe/As combined with 0.7% of alginate system.

This could be described by the species distribution of arsenite (As(III)), arsenate (As(V)), CaFe mixed metal, and pH-dependent forms of charge density on alginate, which could be result in electrostatic repulsion between anionic species of arsenic and carboxylate (-COO$^-$) functional groups on alginate surface, or the competition between anionic species of arsenic and the negatively charged of carboxylate functional groups on alginate surface which can coprecipitate with the ionized form of calcium by electrostatic interaction, result in the decreasing of arsenic removal efficiency. However, the nature or alginate could remove arsenic via bridging mechanism varies on their molecular weight.

Table 4.11 Arsenic removal efficiency by effective combination of mixed metal (MgFe and CaFe) and biopolymer system

As solution (300 mg/L)			%Removal ($M^{2+}M^{3+}$+%ALG)	
pH	Mixed metal	Time (minute)	0% ALG	0.7% ALG
9	1.25MgFe/As	5	66.7 ± 0.2	75.8 ± 1.0
7	1.25CaFe/As		61.3 ± 0.4	65.3 ± 0.9
	1.5CaFe/As		75.2 ± 0.5	80.2 ± 0.4
	2.0CaFe/As		83.4 ± 0.3	91.6 ± 1.0

The combination of mixed metal (MgFe and CaFe) and biopolymer (alginate or chitosan) systems for arsenic removal via coprecipitation process were investigated and reported the results as mentioned in the prior sections. The results showed that the arsenic removal efficiency was increased at pH9 for 0.7%w/v of alginate combine with 1.25MgFe/As, and it also increased at pH7 for 0.7%w/v of alginate combine with 1.25, 1.5 and 2.0 CaFe/As system, which is 4-9% greater than the system without alginate added, at the comparable optimal dosage values of mixed metal, as shown in Table 4.11. Thus, it can be determined that the combined use of mixed metal (MgFe or CaFe) and alginate has synergistic effects according to the enhancement of arsenic removal performance, resulting in the reduction of metal salts (coagulants) needed.

4.4 Application in real industrial wastewater sample

Nevertheless, all of the results suggested that the arsenic removal efficiency using MgFe mixed metal as coagulants is the most effective treatment system via coprecipitation method, by the reason of their high removal efficiency and simplicity of chemical preparation. Consequently, the real industrial wastewater sample from a petrochemical company was suitable to treat by MgFe mixed metal system under their optimal condition.

For evaluation of the efficiency of MgFe mixed metal system for arsenic removal process in real wastewater sample which contains 828 mg/L of arsenic, the treatment of wastewater sample for arsenic removal was divided into 2 parts, including triple dilution of real wastewater with 2.5MgFe/As, and non-dilution of real wastewater with 2.5, 3.0 and 3.5MgFe/As systems, by using the retention time at 0 minute with 400 rpm for speed of stirring. Moreover, the results and discussion of the treatment of real industrial wastewater sample are provided in the following subsections.

4.4.1 Triple-dilution of real wastewater with 2.5MgFe/As

Table 4.12 Arsenic removal efficiency from triple-dilution of real industrial wastewater

pH		Triple-dilution of wastewater (2.5MgFe/As, As 300 mg/L)
9	%RV	94.9 ± 0.1
	Conc. (mg/L)	10.1 ± 0.1

This results from Table 4.12 were obtained by using 2.5MgFe/As at pH9, to evaluate the removal efficiency of arsenic form the triple-dilution of real industrial wastewater sample. The result showed the arsenic removal efficiency from triple-dilution of real industrial wastewater was about 94.9% which approximately to the arsenic removal efficiency from simulated wastewater, 4As(III): 1As(V), which contain 300 mg/L of arsenic via using MgFe mixed metal as shown in the prior section.

4.4.2 Non-dilution of real wastewater with 2.5, 3.0 and 3.5MgFe/As

Table 4.13 Arsenic removal efficiency from non-dilution of real industrial wastewater

pH		Non-dilution of wastewater (As 828 mg/L)		
		2.5MgFe/As	3.0MgFe/As	3.5MgFe/As
9	%RV	92.4 ± 0.2	98.0 ± 0.1	98.5 ± 0.1
	Conc. (mg/L)	12.8 ± 0.2	5.27 ± 0.4	3.83 ± 0.3

This results from Table 4.13 were obtained by varying 2.5, 3.0 and 3.5MgFe/As at pH9, to evaluate the removal efficiency of arsenic from non-dilution of real industrial wastewater sample which approximately contains 828 mg/L of arsenic. The results showed the arsenic removal efficiency from non-dilution of real industrial wastewater were about 92.4%, 98.0% and 98.5% for 2.5, 3.0 and 3.5 MgFe/As, respectively. However, the percentage of arsenic removal via using 2.5MgFe/As was a little less than the arsenic removal percentage from simulated wastewater, which contain 300 mg/L of arsenic, about 3% at the comparable dosage values. It probably due to the fact that real industrial wastewater is not only composed of inorganic arsenic species, but it is also composed of organic arsenic species. Furthermore, the interfering ions might be presented in the real wastewater which results in the decreasing of arsenic removal performance. However, the arsenic removal can be improved by increasing the mole ratio between MgFe mixed metal and arsenic as 3.0 and 3.5MgFe/As for increasing the active sites of metal, and enhancement of arsenic removal efficiency. The results showed that the arsenic removal efficiency was 98.0% and 98.5% via using 3.0 and 3.5MgFe/As as coagulants, consecutively. Moreover, the performance of coprecipitation method via using MgFe mixed metal system for removing of arsenic, was also evaluated in the term of capacity (mg As/ g metal). And the result showed that MgFe mixed metal system can remove arsenic in the real industrial wastewater sample for non-dilution system approximately 407.5, 360.6, and 310.3 mg/g by using in order of 2.5, 3.0, and 3.5MgFe/As.

Therefore, it could be concluded that MgFe mixed metal system can be applied for treatment of arsenic contaminated from the real industrial wastewater sample, and it also represented a good performance in term of high arsenic removal efficiency, and arsenic removal capacity (mg As/ g metal), due to the higher of arsenic removal capacity in real wastewater sample (310.3-407.5 mg/g) compared with the previous work which can remove arsenite (As(III)) and arsenate (As(V)) about 286.9 and 331.1 mg/g) via using MgFe mixed metal system [46], consecutively.

Even though, arsenic was successfully removed by MgFe mixed metal system with a good performance of removal efficiency, but the final concentration of arsenic in the real wastewater sample were approximately obtained as 3.8-12.8 mg/L, which still higher than the Pollution control Department (PCD) guideline value of 250 ppb (0.25 mg/L) for wastewater standard. Therefore, the combination of several treatment methods such as ion exchange, membrane filtration, or adsorption with coprecipitation method was suggested for improving the removal of arsenic from real wastewater sample, to bring down the concentration of arsenic below PCD limit value.

CHAPTER V

CONCLUSION

5.1 Conclusion

Since arsenic pollution has become one of the major environmental problems; thus, several conventional techniques have been developed for arsenic removal from contaminated water. Among all of the techniques, coprecipitation method is one of the most interested methods due to their simplicity, inexpensive, and effective process, and ready availability of chemicals. Therefore, this study reports on the arsenic removal by coprecipitation process with variable combinations of well-known inorganic metal salts, such as ferric chloride ($FeCl_3$) or aluminum chloride ($AlCl_3$) combined with the environmentally friendly inorganic metal salts, such as magnesium chloride ($MgCl_2$) or calcium chloride ($CaCl_2$), which is called “mixed metal system”, as coagulants to precipitate arsenic from wastewater. However, the use of inorganic metal salts or chemical methods, can cause the toxicity to the living organisms from sludge production. Alternatively, the use of biopolymers as flocculants also has useful properties such as large flocs formation and high settling properties. Hence, the coprecipitation techniques which use mixed metal hydroxides as coagulants, or the use of mixed metal salts as coagulants combined with biopolymers (alginate or chitosan) as flocculants were also studied and evaluated in this research, in terms of arsenic removal efficiency, by using inductively coupled plasma optical emission spectrometer (ICP-OES) for determining.

Coprecipitation of arsenic by using mixed metal systems (MgFe, CaFe, MgAl, CaAl) as coagulants, are investigated and reported in this study. The results showed that the arsenic removal efficiency via mixed metal systems which using ferric chloride ($FeCl_3$) as trivalent metal salts (MgFe or CaFe) to precipitate arsenic, was more effective than using aluminum chloride ($AlCl_3$) as trivalent metal salts (MgAl or CaAl) system. Furthermore, the efficacy of coprecipitation method by using mixed metal as coagulants is influenced by various operating parameters including pH of the solution, M^{2+}: M^{3+} mole ratio, $M^{2+}M^{3+}$: As mole ratio, step of pH adjustment, retention time, and speed of stirring. The factors affecting on arsenic removal via using mixed metal were studied by batch system, then the optimal conditions for effective removing of arsenic are concluded in Table 5.1.

Table 5.1 Arsenic removal efficiency by using optimal condition of mixed metal systems

Simulated wastewater (300 mg/L of As)				
System	Factor	Optimal condition	%RV (MgFe)	%RV (CaFe)
MgFe or CaFe	pH	9	95.4 ± 0.0	96.8 ± 0.1
	M^{2+}: M^{3+}	0.5: 1		
	$M^{2+}M^{3+}$: As	2.5: 1		
	Step of pH adjustment	Metal pre-added		
	Retention time (min)	0		
	Speed of stirring (rpm)	400		

Moreover, the synergistic effect of mixed metal (MgFe or CaFe) combined with biopolymer (alginate or chitosan) systems were also studied and investigated for finding the optimum amount and condition for effective arsenic removal treatment process. The results showed that the arsenic removal efficiency of the combination between mixed metal and biopolymer system depends on various parameters such as, type and concentration (%w/v) of biopolymers, retention time, and pH of the solution which results in the different speciation of metal ions, or charge density of biopolymers. The optimum amount and condition of the combination between mixed metal and biopolymer systems for effective arsenic removal are concluded in Table 5.2.

Table 5.2 Arsenic removal efficiency by using optimal condition of mixed metal combine with biopolymer systems

Simulated wastewater (300 mg/L of As)				
pH	**Mixed metals**	**Alginate Conc. (%w/v)**	**Retention time (min)**	**%RV ($M^{2+}M^{3+}$+ALG)**
9	**1.25MgFe/As**	**0.7**	**5**	75.8 ± 1.0
7	**1.25CaFe/As**			65.3 ± 0.9
	1.5CaFe/As			80.2 ± 0.4
	2.0CaFe/As			91.6 ± 1.0

For the combination of mixed metal and biopolymer systems as shown in Table 5.2, the results showed that the arsenic removal efficiency were increased at pH9 for 0.7%w/v of alginate combine with 1.25MgFe/As, and it also increased at pH7 for 0.7%w/v of alginate combine with 1.25, 1.5 or 2.0CaFe/As system, which is 4-9% greater than only mixed metal (MgFe or CaFe) system, at the comparable optimal dosage values. Therefore, it can be determined that the combined use of mixed metal and alginate has synergistic effects according to the enhancement of arsenic removal efficiency, resulting in the reduction of metal salts (coagulants) needed.

All the results suggested that using MgFe mixed metal as coagulants is the most effective treatment system for arsenic removal from simulated wastewater via coprecipitation method, due to their high of arsenic removal efficiency, and simplicity of chemical preparation. Therefore, the real industrial wastewater sample was suitable and applicable to treat by MgFe mixed metal system under their optimal conditions.

Finally, the real industrial wastewater sample from a petrochemical company, which contains 828 mg/L of arsenic was successfully treated by coprecipitation method for arsenic removal, via MgFe mixed metal system with the optimum conditions. And the results showed the arsenic removal efficiency from real industrial wastewater were about 94.9% for triple dilution of wastewater with 2.5MgFe/As (As 300 mg/L) mixed metals system, 92.4%, 98.0%, and 98.5% for non-dilution of wastewater by using 2.5, 3.0 and 3.5MgFe/As (As 828 mg/L) mixed metals system, consecutively. Therefore, it could be concluded that mixed metals system represented good performance when applied to the real industrial wastewater sample in terms of arsenic removal efficiency, as shown in Table 5.3.

Table 5.3 Arsenic removal efficiency from real industrial wastewater sample

Real industrial wastewater (828 mg/L of As)				
pH	**Triple-dilution**	**Non-dilution**		
9	**2.5MgFe/As**	**2.5MgFe/As**	**3.0MgFe/As**	**3.5MgFe/As**
	94.9 ± 0.1	92.4 ± 0.2	98.0 ± 0.1	98.5 ± 0.1

5.2 Suggestions for future work

- Apply the combination of several treatment methods such as oxidation, ion exchange, membrane filtration, or adsorption with coprecipitation method for completing the removal of arsenic from real wastewater, to produce clean water which is suited for the reuse applications.

- Apply the most effective treatment system with an optimum amount and condition to remove arsenic contaminated in large-scale for industrial wastewater treatment plant applications.

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