CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Arsenic

2.1.1 Arsenic element

Arsenic is a metalloid element in the periodic table. It is tasteless and odorless (atomic number 33, symbol As in the periodic table) [15]. It can contaminate in water from natural deposits in the earth. or from operations that use high dose arsenic implants. The toxicity of arsenic causes poisoning and death.

2.1.2 Arsenic compounds

Naturally, arsenic occurs in water, soil and environment in both inorganic and organic compounds that are shown in Table 2.1 and Figure 2.1. The forms of arsenic are sensitive with the redox state and pH of the chemical environment. The oxidation state of arsenic has five states; i.e. -3 (arsine gas, AsH_3), -1 (alkyl arsenic), 0 (arsenic element), +3 (arsenite) and +5 (arsenate). For inorganic compounds, arsenic atom binds. with oxygen and hydrogen atoms to form oxyanions similar to many non-metals. For organic compounds, arsenic binds to carbon atoms that mainly compose in molecules such as methylarsenic and dimethylarsenic acid [13].

The inorganic arsenic, reduced form (arsenite, As(III)) and oxidized form (arsenate, As(V)), can be absorbed and accumulated in tissues and body fluids. In the liver, the metabolism of arsenic is about enzymatic and non-enzymatic methylation, the mostly excreted metabolite in the urine of mammals is dimethylarsenic acid (or Cacodylic acid, DMA(V)). Dimethylarsenic acid and its sodium salt is known as Agent Blue that was used as herbicide for killing rice in the American war in the South-East Asian country of Viet Nam [16].

Table 2.1 Arsenic compounds in the environment [17]

| Name	abbreviation	molecular formular
Arsenite (arsenous acid)	As^{III}, As(III)	$As(OH)_3$
Arsenate (arsenic acid)	As^{V}, As(V)	$AsO(OH)_3$
Monomethylarsonic acid	MMA^{V}, MMAs(V)	$CH_3AsO(OH)_2$
Monomethylarsonous acid	MMA^{III}	$CH_3As(OH)_2$
Dimethylarsinic acid	DMA^{V}, DMAs(V)	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	DMA^{III}, DMAs(III)	$(CH_3)_2AsOH$
Dimethylarsinoyl ethanol	DMAE	$(CH_3)_2AsOCH_2CH_2OH$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Tetramethylarsonium ion	Me_4As^{+}	$(CH_3)_4As^{+}$
Arsenobetaine	AsB	$(CH_3)_3As^{+}CH_2COO^{-}$
Arsenobetaine 2	AsB-2	$(CH_3)_3As^{+}CH_2CH_2COO^{-}$
Arsenochline	AsC	$(CH_3)_3As^{+}CH_2CH_2OH$
Trimethylarsine	TMA^{III}	$(CH_3)_3As$
Arsines	AsH_3, $MeAsH_2$, Me_2AsH	$(CH_3)_xAsH_{3-x}$ (x = 0-3)
Ethylmethylarsines	Et_xAsMe_{3-x}	$(CH_3CH_2)_xAs(CH_3)_{3-x}$ (x = 0-3)
Phenylarsonic acid	PAA	$C_6H_5AsO(OH)_2$
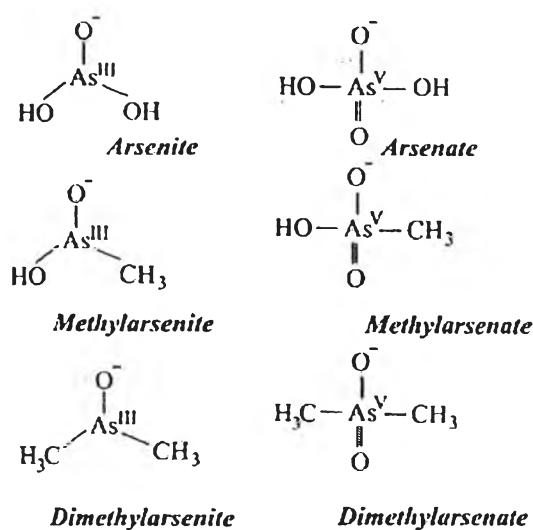
Figure 2.1 Arsenic compounds in water [4]

As mentioned above, the forms of arsenic could be changed with the pH of solution as shown in Figure 2.2. For example, arsenite (As(III)), at solution pH < 7 occurs in H_3AsO_3 that is neutral molecule while, arsenate (As(V)) appears in $HAsO_4^{2-}$, $H_2AsO_4^-$ that has negative charge, and neutral H_3AsO_4 molecule.
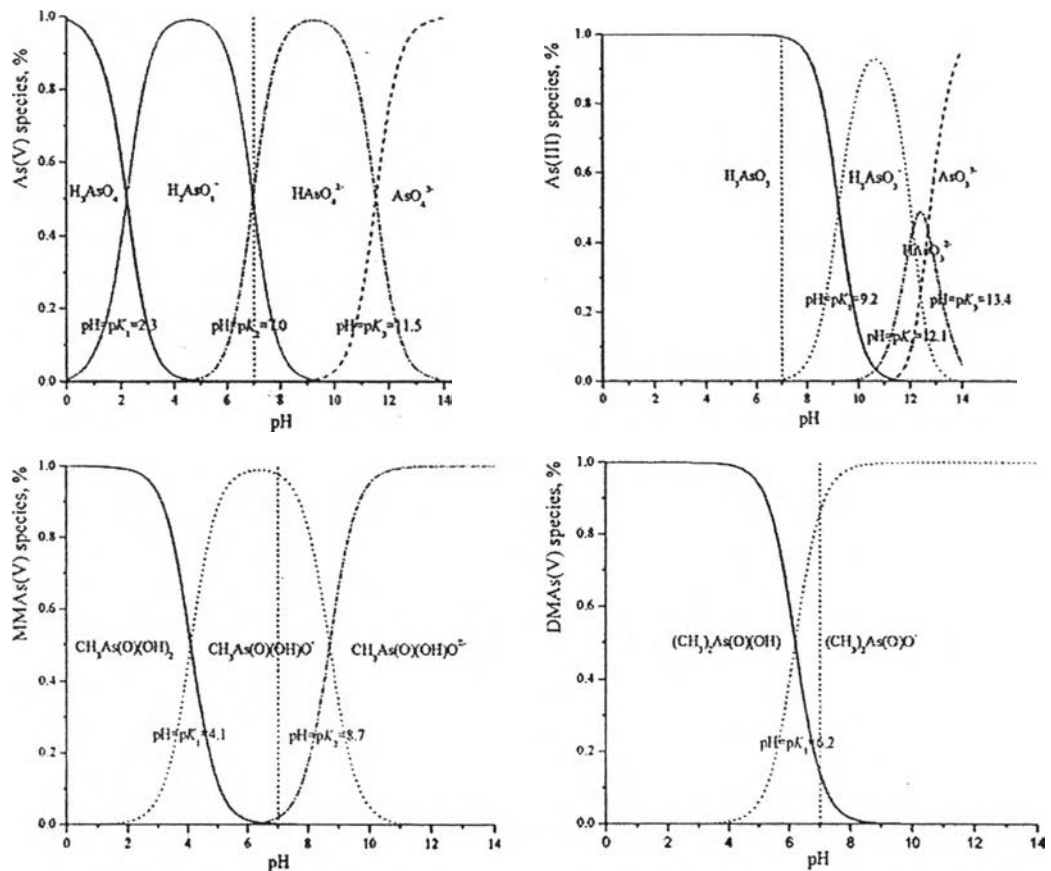

Figure 2.2 Arsenic forms of arsenate, arsenite, methylarsenic acid and dimethylarsenic acid at different pH of solution [18].

The presence of arsenic contaminated in water is related to the processing of a variety of ores such as copper, gold, nickel, lead, and zinc, and including the manufacture of pesticide, pigment, electronic component, glass, alloy and pharmaceutical that used arsenic as active ingredients. Thus, arsenic from these processing can be released into natural water. Furthermore, inorganic arsenic is commonly found at high levels in groundwater of a number of countries and highly

toxic while, organic arsenic compounds (such as those found in seafood) are less harmful to health.

2.2 Method of removal of arsenic from wastewater

Industries that highly used arsenic should efficiently remove arsenic from wastewater before disposal into environment. Because the production of drinking water brings the raw water from environment, especially people who live in area next to arsenic rock or other industrial pollution, used groundwater in their daily-life without purify process. They have health damages caused by an intake high concentration of arsenic, especially in South Asia [19]

Hence, the removal method for arsenic in wastewater is an important process to control the amount of arsenic to be below the standard maximum arsenic contaminant level. Some important methods are discussed below.

2.2.1 Oxidation

Generally, the inorganic forms of arsenic are often found in wastewater. The most removal processes of arsenite, As(III) and arsenate, As(V) are effective to remove arsenate only, but not arsenite, because general form of arsenite is a non-charged form at pH value below 9.2. Therefore, the method for removal of arsenite needs an oxidation step for converting arsenite to arsenate [20].

Oxidation is the chemical reaction for adding the oxygen atom to a compound or the reaction involving the loss of electrons from a compound. The chemicals for using in oxidation process include hypochlorite, permanganate, hydrogen peroxide and chlorine. In addition, the photochemical oxidization processes from the reaction of radiant energy can be used. These can convert arsenite to arsenate and adsorb on iron and manganese (Fe/Mn) hydroxides, since both iron and arsenic are oxidized at the same time during iron precipitation. However, the oxidation alone does not remove arsenic from solution but the process must be combined with an arsenic removal process such as oxidation filtration technologies [21].

2.2.2   Coagulation, precipitation and filtration

Coagulation followed by precipitation and filtration is commonly used for removal of arsenic from wastewater. This process, commonly referred to coagulation–flocculation-filtration is a technique to reduce a wide range of concentration of arsenic in wastewater to accord with maximum concentration level (MCL).

Coagulation is a technique for removal of impurities in suspended or colloidal forms including inorganic and organic compounds in wastewater. The commonly used chemical coagulants for removal of arsenic are ferric chloride, aluminium sulfate, polyaluminium chloride and polyvinylsulfonic acid, etc. These chemicals are added into water, they dissolve under efficient stirring for one to few minutes. During this flocculation process, all kinds of micro-particles and negatively charged ions are attached to the floc by electrostatic attachment. Arsenic is also adsorbed onto coagulated floc. After that, the precipitate can be removed partially by mean of precipitation, and then filtration technique may be required to ensure complete removal of all precipitates. Arsenic removal by coagulation is mainly controlled by pH and coagulant dose. Hence, coagulant type and dosage, pH, water composition were found to be important factor that affected the arsenic removal efficiency [20].

2.2.3   Ion-exchange

Ion exchange is frequently used as a treatment method for arsenic removal in wastewater. Arsenic contaminated water is passed through the resin bed, the contaminant arsenic ions have exchanged with the other ions of the resin. Strong base anion exchange resins are commercially available that can effectively remove arsenate from water, while arsenite being non-charged form, is not removed. Therefore, an oxidation step to convert arsenite to arsenate is necessary in the process. In general, sulfate-selective resins are particularly suited for arsenate removal. Nitrate-selective resin is also a choice in arsenic removal.

Prior to ion exchange process, wastewater should be pre-treated such as by filtration to remove organics, suspended solids, and other contaminants that can foul the resins and reduce their effectiveness [20]. Ion exchange resins must be

periodically regenerated to remove adsorbed contaminants and replenish the exchanged ions. Regeneration solution and spent resin have highly content of arsenic. They would require an additional treatment before disposal or reuse. Furthermore, as the resin exhausted, it can be regenerated by washing with a NaCl solution.

2.2.4   Reverse osmosis

Reverse osmosis is a method for removal of impurities in wastewater using membrane separation process. Water is forced through a membrane. Then, the contents of the water, many different kinds of dissolved solids such as heavy metal, including arsenic, are left behind on the membrane, while treated water passes through [22]. However, the membrane can readily be fouled by oil, grease, and suspended solids. Moreover, reverse osmosis technique is usually expensive. Hence, it is recommended for the application such as purification of water for medical and industrial purpose, desalination, brackish water conversation and for removal of specific ions, etc.

2.2.5   Biological process

For biological process, arsenic in wastewater can be removed by microorganisms. Microorganisms are mostly specific bacteria being capable to remove arsenic compounds in wastewater by oxidation/reduction, mineralization, detoxification or methylation. The crucial factor in biological process includes energy, carbon source and the suitable conditions such as temperature and pH value [23].

2.2.6   Adsorption

Adsorption is a technique that uses a solid for removing arsenic substances from gaseous or liquid solution accumulated onto the surface of porous solid. The widely used solid for arsenic removal include [24];

- Activated carbon
- Polymeric adsorbent
- Activated alumina
- Granular ferric hydroxide/oxide

- Zeolite
- Ion exchange resins

The effectiveness of arsenic removal by adsorption onto the surface of adsorbent depends on the surface area of solid. Hence, the first step for characterization of adsorbent is estimation of its surface area and polarity.

2.3 Adsorption process

Adsorption is a process that substances being atoms, ions, bimolecules or molecules (adsorbate) from gas or liquid phase are accumulated onto a surface of solid substrate (adsorbent) via mass transfer process.

2.3.1   Adsorption mechanism

Adsorption mechanism is a mass transfer process of an adsorbate or analyte transferring from gas or liquid medium to porous adsorbent that some steps in adsorption process are fast and some are slow. Furthermore, the slowest steps in adsorption process is the rate determining step of the process. Thus, the slowest step in adsorption process is important. For the adsorption process, it consists of three steps including [25];

I.   Bulk transport, a process that an analyte transfers from bulk solution to the surface of liquid layer which cover the surface of adsorbent. Bulk transport process occurs very quickly.

II.   Surface transport or film transport, an analyte transfers from a liquid layer to the surface of adsorbent. This step is called external diffusion or film diffusion.

III. Intraparticle transport or pore diffusion, an analyte at the surface of adsorbent diffuse into the pores of adsorbent. This process is called internal diffusion. After that, adsorption occurs by adhesion of analyte onto pores of adsorbent

IV.   The efficiency of adsorption process depends on many conditions such as the surface area and particle size of adsorbent, contact time, temperature, pH of solution and initial concentration of

analyte. Moreover, the adsorption process is usually classified to physisorption and chemisorption.

2.3.2   Physical adsorption or physisorption

Physical adsorption occurs by the van der Waal's interaction between analyte and the surface of adsorbent. This interaction is weak electrical attractive force [26]. Physical adsorption is a theory for determining in adsorbed molecule forming multiple layers. The concentration of analyte has an effect on a quantity of layers. In physical adsorption, the analyte can be adsorbed on all the area of adsorbent surface when the conditions of adsorption are suitable such as temperature and charge. However, this kind of adsorption can be easily reversible.

2.3.3   Chemical adsorption or chemisorption

This adsorption is a result from the sharing of electrons between an analyte and the functional group on the surface of adsorbent as chemical bond. Thus, chemisorption is stronger than the interaction in physisorption. The analyte can contact directly with the surface and form a single-layer on the surface. Moreover, the chemical adsorption is irreversible or sometimes slightly reversible.

2.4 Adsorption equilibrium and adsorption isotherm

In adsorption process, an analyte can be adsorbed on the surface of adsorbent and desorbed in solution at the same time until the equilibrium is reached or the concentration of analyte on the surface of adsorbent does not change. This process is called adsorption equilibrium. At adsorption equilibrium, the relationship between the capacity of adsorption and the remaining of analyte concentration in solution at room temperature is called the "adsorption isotherm". It is the information for discussing the phenomenon of adsorption. The commonly used mathematic models are Langmuir and Freundlich models for determination of the phenomenon of adsorption [27].

2.4.1   Langmuir isotherm

Langmuir isotherm is used for determination of the adsorption process in a monolayer of adsorbent surface at a constant temperature. Furthermore, all adsorption occurs through the same mechanism and the enthalpy of adsorption is the same for all molecules of analyte independently of how many have been adsorbed [27]. However, this adsorption is limited with the quantity of analyte. The form of the Langmuir isotherm is shown in Equation 2.1 and 2.2:

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{2.1}$$

$$\frac{C_e}{q} = \frac{1}{b g_m} + \frac{C_e}{q_m} \tag{2.2}$$

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

q_e = the adsorption capacity at equilibrium (mg/g)

q_m = the maximum adsorption capacity (mg/g)

b = a constant related to the free energy of adsorption (L/mg).

In Figure 2.3, when plotting between $\dfrac{C_e}{q}$ value (y axis) and C_e value (x axis), the slope and intercept are $\dfrac{1}{q_m}$ and $\dfrac{1}{b q_m}$ following Equation 2.2. Thus, the q_m and b value can be calculated from the graph.
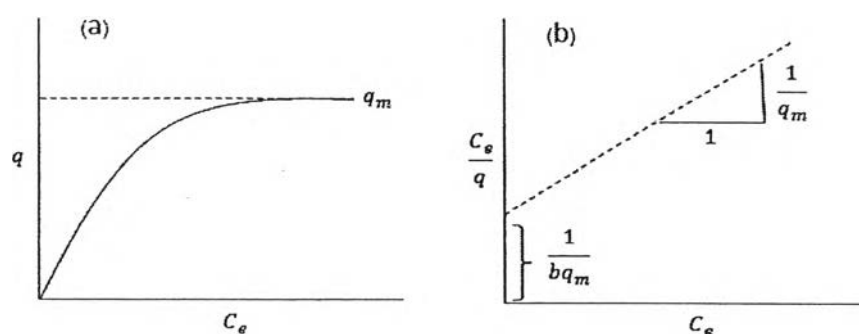

Figure 2.3 The phenomenon of adsorption in a monolayer of surface adsorbent (a) and linear plot (b) of Langmuir adsorption isotherm.

2.4.2 Freundlich isotherm

The Freundlich isotherm is developed from the Langmuir isotherm. The Freundlich model is used for assuming the adsorption of solutes on multilayer surface of adsorbent [27]. The Freundlich isotherm represents an empirical model, while the Langmuir isotherm has a theoretical justification. The Freundlich isotherm is expressed by Equations 2.3 and 2.4.

$$q = K_f C_e^{\frac{1}{n}} \tag{2.3}$$

$$\log q = \log K_f + \frac{1}{n}\log C_e \tag{2.4}$$

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

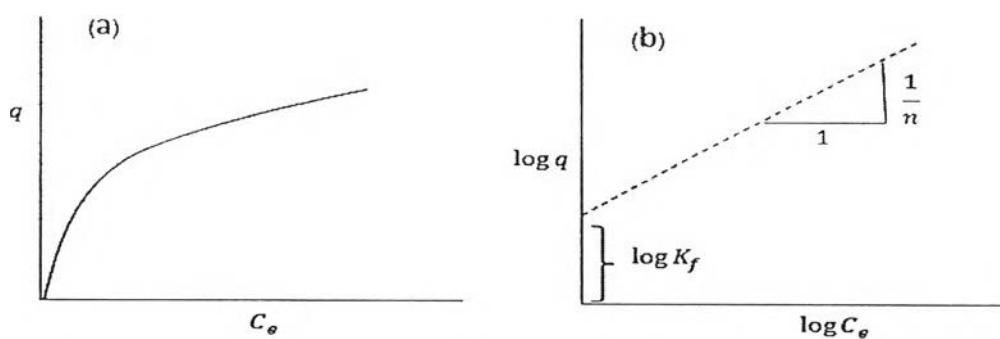n = Freundlich constant related to adsorption intensity

Figure 2.4 The phenomenon of adsorption in multilayer of surface adsorbent (a) and linear plot (b) of Freundlich adsorption isotherm.

2.4.3   BET Adsorption Isotherm

BET adsorption stands for Brunauer – Emmett – Teller adsorption. This isotherm is a model developed from Langmuir equation to describe a multilayer adsorption [27]. The BET isotherm is shown in Equations 2.5.

$$q_e = \frac{q_m b C_e}{(C_s - C_e)[1 + (b-1)(C_e - C_s)]} \tag{2.5}$$

where, q_e = the adsorption capacity at equilibrium (mg/g)

q_m = the maximum adsorption capacity (mg/g)

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

C_s = the saturation concentration of analyte in solution (mg/L)

b = a constant related to the free energy of adsorption (L/mg)

This isotherm assumes that an analyte is adsorbed on the surface of adsorbent in multilayer. The assumptions are listed below:

- Adsorbed analytes are arranged in multiple layers on the surface of adsorbent

- Adsorbed analytes do not move on the surface of adsorbent

- Each layer does not need to be completed before the next layer starts to fill up

- Enthalpy of this adsorption is the same for any layer

- All adsorbed analytes in layers other than the first have the same adsorption energy.

From Equation 2.5, it can be rearranged to give Equation 2.6 as followed:

$$\frac{C_e}{q_e(C_s - C_e)} = \left(\frac{1}{bq_m}\right) + \left(\frac{b-1}{bq_m}\right)\left(\frac{C_e}{C_s}\right) \tag{2.6}$$

From Figure 2.5, when a graph plotting between $C_e/q_e (C_s - C_e)$ and (C_e/C_s) is constructed that the values of b and q_m can be calculated using the slope and intercept of the linear plot following Equation 2.6.
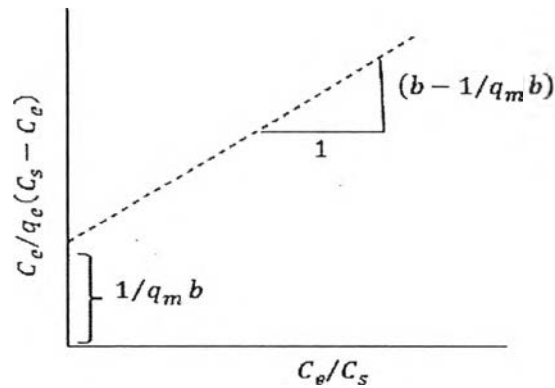
Figure 2.5 The linear plot of Brunauer-Emmett-Teller (BET) adsorption isotherm.

2.5 Adsorption kinetics

The adsorption kinetics describes a substance (or analyte) uptake rate at the solid- liquid interface.

2.5.1   Pseudo-first order kinetics

The pseudo-first order equation is demonstrated by the following Equation 2.7:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (2.7)$$

where q_t = the adsorption capacity at any time (mg/g)

q_e = the adsorption capacity at an equilibrium (mg/g)

k_1 = the rate constant of the pseudo first order adsorption (min^{-1})

The value of $\log(q_e - q_t)$ is linearly correlated with t (Figure 2.6 (a)). The k_1 and q_e are calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ against t as expressed in Equation 2.7.

2.5.2   Pseudo-second order kinetics

The pseudo-second order kinetics equation is present by the following Equations 2.8 to 2.11

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2.8}$$

$$\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + k_2 t \tag{2.9}$$

$$h = k_2 q_e{}^2 \tag{2.10}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{2.11}$$

where q_t = the adsorption capacity at any time (mg/g)

q_e = the adsorption capacity at an equilibrium (mg/g)

k_2 = the rate constants of the pseudo second order adsorption
(g mg^{-1}min^{-1})

h = initial sorption rate constant (mg g^{-1} min^{-1})

The value of $\dfrac{t}{q_t}$ is linearly correlated with t (Figure 2.6 (b)). The k_2 and q_e values are calculated from the slope and intercept of the plot of $\dfrac{t}{q_t}$ against t following Equation 2.10

The parameters from the equations can predict an order of kinetics, a design of sorption system and a behavior of sorption process.
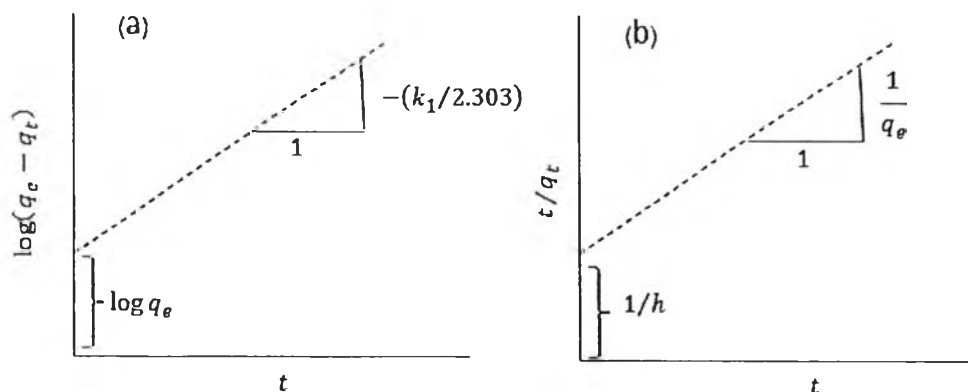

Figure 2.6 (a) pseudo-first order and (b) pseudo-second order kinetics [28].

2.6 Tap water production

Tap water is a necessary factor for human living that includes taking a bath, cleaning, drinking, cooking and the others. Moreover, industry and agricultural sector have to use tap water for processing. Tap water production is a process for removal of suspended solids, microorganisms and toxic chemicals to follow the maximum concentration level (MCL) to ensure safety for human being. In general, tap water production has an appropriate treatment for removal of those contaminants that include [29];

I.   Raw water: The tap water production brings raw water from natural water sources to produce tap water such as rivers, lakes and groundwater. Raw water is pumped from these sites to the treatment plant for processing. Groundwater requires less treatment than water from rivers and lakes.

II.   Coagulation and flocculation: The first step for removal of the dirt and other particles suspended in water is coagulation and flocculation. The chemical agent (coagulant) is added into raw water. There is alum, iron salt and synthetic organic polymer. Then, a positive charge of coagulant neutralizes the negative charge of dirt and other particles in the water. After that, these particles bind with coagulant and form larger particles; called floc. It will be the heavy weight particle and precipitate to the bottom of tank.

III. Sedimentation: The sedimentation is the process that floc settles to the bottom of the water tank due to its weight. The solid residues are called sludge.

IV.   Filtration: The clear water on the top of tank will pass through the filters such as sand, gravel, charcoal and the other filter in special contaminants. Due to some particles or dissolved matters remaining dissolve in water such as dust, iron and manganese. Therefore, the filtration process can remove these particles before the disinfection process.

V.   Disinfection: Chlorine or some other suitable methods are used to kill any remaining microorganism in water after filtration process such as parasites, bacteria, viruses and other microorganisms.

VI.   Water quality and storage: The quantity of tap water is examined that including the pH value, turbidity, chemical concentration and microorganism in order to confirm the safety of tap water before consumption. And then, water is kept in a closed reservoir at high location for flowing passes the pipe of community. A schematic presentation of tap water production is predicted in Figure 2.7.
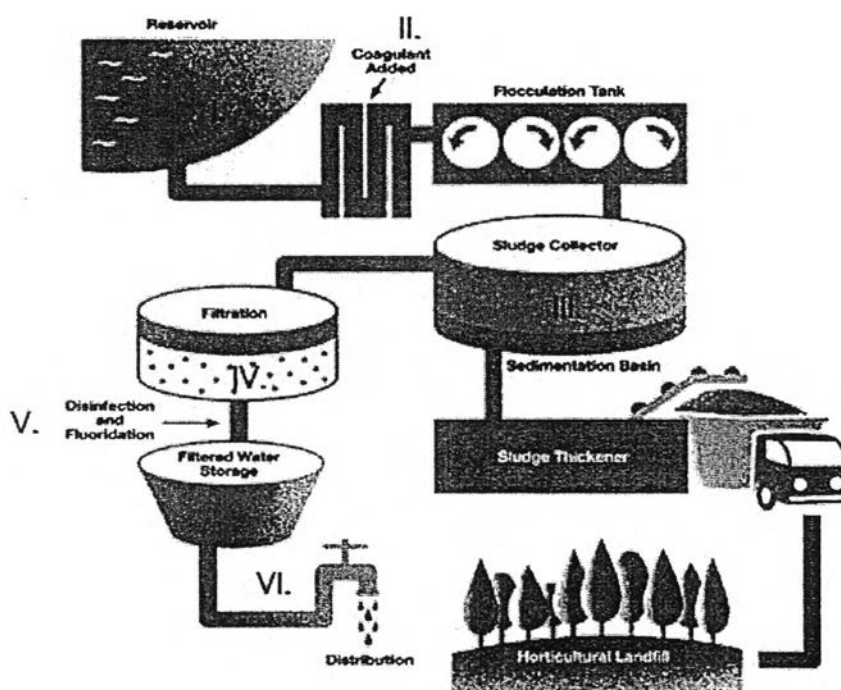

Figure 2.7 The picture showed the tap water treatment process and sludge as a by-product during process [29].

2.7 Sludge from tap water production (STWP)

Sludge from tap water production (STWP) is a by-product of water treatment process during sedimentation. Therefore, the sludge contains mainly aluminium and

iron hydroxides remaining from the coagulation process. Since aluminium sulfate, alum $(Al_2(SO_4)_3.18H_2O)$ and polyaluminium chloride are widely used as coagulant compounds. Then, they were added to water in the presence of alkalinity [30]. It can provide aluminium hydroxide as described by the following chemical reaction.

$$Al_2(SO_4)_3.18H_2O + 3Ca(OH)_2 \longrightarrow 3CaSO_4 + 2Al(OH)_3 + 18H_2O$$

While, ferric salts $(FeCl_3, Fe_2(SO_4)_3)$ are also used as coagulant compounds that can produced ferric hydroxide at pH 3-13 during the coagulation process.

$$Fe^{3+} + OH^- \longrightarrow Fe(OH)_3$$

Aluminium and iron hydroxides in sludge are highly porous material and have a strong affinity for anionic species. Additionally, arsenic in wastewater can be remediated by adsorption onto aluminium and iron hydroxide sludge by surface complexation (ligand exchange or inner-sphere complex formation) on the surface of adsorbent [31-33]. However, the adsorption of arsenic onto aluminium and iron hydroxides is complicated to understand. Thus, the adsorption phenomenon usually described using standard isotherm models such as the Langmuir and Freundlich isotherms.
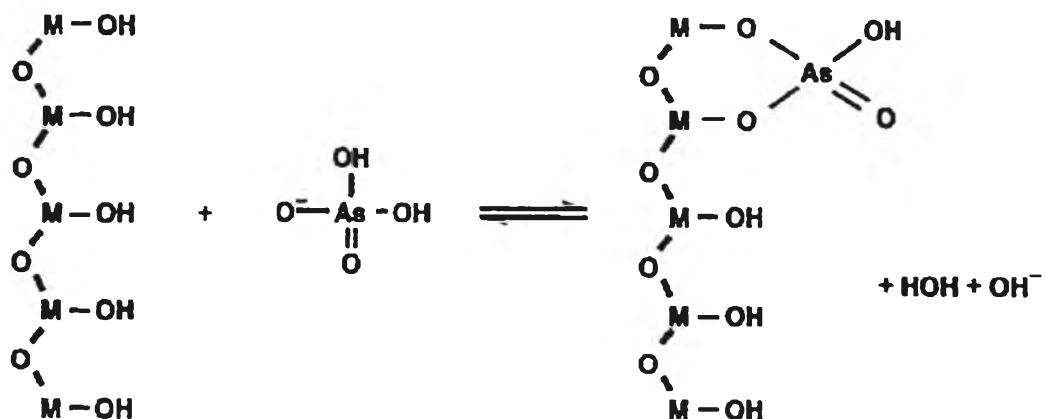

Figure 2.8 Mechanism of arsenate ligand exchange on the surface of metal oxohydroxides [32].

2.7.1   Sludge treatment

The sludge treatment is a process to reduce the volume and weight of sludge, the amount of organic constituents, the disease-causing microorganisms and odour compounds that can found in the sludge. The advantage of sludge treatment is easier and reduces the cost for transportation of sludge. Accordingly, this treatment includes thickening, stabilization, conditioning and dewatering [34].

I.   Thickening: the first process of sludge treatment for increasing sludge concentration by sedimentation.

II. Stabilization: to reduce organic matter in sludge using aerobic and anaerobic microorganism digestion for decreasing stinking-smell of sludge.

III. Conditioning: to improve the properties of sludge to be suitable before utilizing or disposing.

IV. Dewatering: to eradicate the water in sludge for reducing the weight and volume of sludge in order to easier trucking sludge.

After that, the treated sludge must be disposed or utilized properly such as landfill, incineration, agriculture application and incorporate with construction material.

2.8 Management of sludge wastes containing arsenic

Arsenic cannot loss from the environment. It can only be converted into different forms or transformed into insoluble compounds by combination with other element. Therefore, we can only manage any arsenic waste to be safe disposal that arsenic cannot return to contaminate the environment in long-term. The method for disposal sludge wastes containing arsenic includes[13];

2.8.1   Landfill

Landfill is a widely employed method of arsenic containing sludge disposal and used in many places around the world. The high water content of arsenic sludge from adsorption process increases a bulk of waste. Thus, raw arsenic sludge is often air dried before disposal. This method requires the extensive and safe

space for hazardous waste site. Moreover, arsenic sludge can be dumped into small sand covered brick-lined pits.

2.8.2 Incineration

Incineration is a process using firing the sludge at high temperature in enclose structure. This process reduces mass of sludge to ash that is less than the original volume. Sludge incineration can destroy pathogens and toxic organic chemicals that effect to health. However, incineration is high cost and limit with arsenic sludge because of arsenic containing compound may be volatile to the environment.

2.8.3 Stabilization/solidification (S/S)

Stabilization/solidification technique is a process that mixes the arsenic sludge into a cementitious binder system. This technique is normally used before landfill waste treatment that aims to make hazardous waste safe for disposal. The purpose of this process is encapsulated or fixation and incorporates the waste into the binder system in order to prevents the arsenic compound enter the environment. A number of stabilization/solidification binders specifically for arsenic have been investigated including [14];

- Portland cement
- Portland cement and iron
- Portland cement and lime
- Portland cement and fly ash
- Portland cement and silicates

Many research reported that the stabilization/solidification of arsenic sludge is successful when cement, cement and iron, cement and lime are used as cementitious binders.

2.9 Metropolitan waterworks authority, Thailand

The sludge from Metropolitan Waterworks Authority, Bangkhen, Thailand was used to be arsenic adsorbent in wastewater. Furthermore, this waterworks produces

tap water around 3.6 million m^3/day using raw water that is pumped from the Chao Phraya River into the water treatment facilities. Then, coagulants for impurity removal from raw water are commonly used including;

- Powder aluminium sulfate
- Liquid aluminium sulfate
- Powder polyaluminium chloride
- Liquid polyaluminium chloride
- Ferric chloride

Hence, the sludge is generated during coagulation process around 75-105 tons/day. This makes waterworks to pay much expense for sludge disposal 11 million Baht/year. Accordingly, this research focus on a recycle of sludge from coagulation process to be an alternative low-cost adsorbent for arsenic removal in order to worthwhile utilize the sludge before disposal [35].

Figure 2.9 Sludge from the Metropolitan Waterworks Authority (Bangkhen, Thailand).

2.10 Literature review

Arsenic in wastewater can be removed by typical physical and chemical methods such as oxidation, precipitation, ion exchange and reverse osmosis. However, these processes are high costly and complicated to work. For adsorption process, it is easier and cost-effective for arsenic removal from wastewater. Hence, several researchers are interested in using adsorption technique for examination of

arsenic removal. There are activated carbon, activated alumina and granular ferric hydroxide used as arsenic adsorbent. Besides of this, iron oxide mineral (iron rich laterite soil, goethite, magnetite and hematite) [36], iron-oxide coated sands [37] and iron-oxide-coated polymeric materials [38] have demonstrated as efficient adsorbent for arsenic. Nevertheless, these adsorbents still have many steps of preparation and resulting in high cost for using. Consequently, many studies focused on searching the alternative low-cost alternative adsorbents that are efficient and easier for arsenic removal.

2.10.1 Arsenic removal from water by low-cost adsorbent

Many researchers studied arsenic removal in aqueous solution by recycling solid waste, some of them are summarized as followed:

Diamadopoulos et al. (1993) [39] used fly ash, a by-product occurred from coal power stations for arsenate (As(V)) removal in water. The major composition of fly ash was CaO, observed by X-ray fluorescence spectrometer. Surface area of fly ash was found to be 0.8 m^2/g. Moreover, the optimum pH for arsenate removal in water was 4.

Namasivayam et al. (1998) [40] recycled an industrial solid waste as arsenate adsorbent. Fe(III) and Cr(III) hydroxides were mostly found in the solid waste. The effects of arsenic adsorption including pH, initial arsenic concentration, agitation time, adsorbent dosage and adsorbent particle size were studied. In addition, the arsenate adsorption kinetics followed pseudo-first order equation. The maximum arsenate adsorption capacity was 11.02 mg As/g solid.

Altundogan et al. (2000) [41] used red mud that was a solid waste from bauxite processing as alternative arsenic adsorbent in aqueous solution. The experimental result showed that arsenite (As(III)) was efficiently removed in alkaline condition, whereas the adsorption of arsenate (As(V)) was favorable in acidic pH range (1.1-3.2). The equilibrium time for arsenite (As(III)) and arsenate (As(V)) removal were 45 and 90 minutes, respectively. In addition, the adsorption isotherms of both arsenite (As(III)) and arsenate (As(V)) were well fitted with Langmuir isotherm model.

Thermodynamic study based on the data from various temperature experiments indicate that As(III) adsorption was exothermic, while As(V) adsorption was endothermic.

Goh et al. (2004) [42] studied the adsorption of As(III), As(V), Se(IV), and Se(VI) on a tropical soil as adsorbent. The effects of contact time, pH, competing anion at various concentrations on both As and Se adsorption were examined. In batch study, the sequence of As and Se adsorption capacity was As(V) > Se(IV) > As(III) > Se(VI). Adsorption kinetics was best described by the Elovich equation. Furthermore, adsorption isotherms of As(III) and Se(VI) were fitted with Langmuir model, whereas As(III) and Se(VI) favored more in line with Freundlich model.

Fan et al. (2008) [43] developed the waste ash from a power plant fueled with municipal solid waste and coal located in China as a new arsenate (As(V)) adsorbent. Firstly, ash was hydrothermal treatment for zeolite synthesis and modified with iron (II) ion by agitation (ISZ) and ultrasonic (UISZ) method. The influences of pH, initial arsenate concentration, contact time and adsorbent dosage were studied. The result showed that the adsorption isotherms were fitted with Langmuir isotherm which allowed the calculation of the maximum adsorption capacity of UISZ and ISZ was 13.04 and 5.37 mg/g, respectively. Additionally, the leaching of hazardous element was also elucidated.

Oliveria et al. (2008) [44] evaluated the ability of using a solid waste from the leather industry as Cr(VI) and As(V) adsorbent. The characterization of solid waste was performed by chemical analyses, infrared spectroscopy and scanning electronic microscopy (SEM) in order to studied its properties. Moreover, the result indicated that Cr(VI) and As(V) adsorption occurred by monolayer adsorption process on the surface of adsorbent. The maximum Cr(VI) and As(V) adsorption capacities were 133 and 26 mg/g, respectively.

Maiti et al. (2008) [45] investigated the efficiency of untreated natural laterite (NL) as adsorbent for arsenate ion removal from water. In batch study, the

effects of adsorbent dose, pH of solution, ionic strength, initial arsenate concentration, temperature, and contact time were examined. The optimal pH for arsenate removal was in the range of 5.5 to 7.5. The adsorption isotherm showed a good compliance with Langmuir isotherm model, and the maximum adsorption capacity at 315 K was found to be 0.565 mg/g. In addition, column study using a fixed bed was also studied using the Adams-Bohart model for predicting the breakthrough curve in column study.

2.10.2 Heavy metal and other compound removal from water by sludge

In recent years, several groups of researchers have demonstrated the use of sludge as low-cost adsorbent for heavy metal and other compounds that contaminated in water including;

Chu (1998) [46] studied alum sludge for lead removal in synthetic lead wastewater. The pH of 11.6 was suggested for lead removal due to the fact that lead hydroxide can precipitate with alum sludge in alkaline conditions. After that, the efficiency of lead removal increased from 82 to 90% when fresh alum was added into the alum sludge.

Liu et al. (2006) [47] examined the effect of temperature, initial concentration of Cr(VI) and particle size on Cr(VI) removal using wine processing waste sludge (WPWS). In addition, few aromatic compounds with carboxylic groups which could interact with chromium species by protonation and redox reaction were demonstrated. The kinetics of Cr(VI) adsorption on WPWS was fitted with a pseudo-second order kinetic model.

Choi et al. (2006) [48] studied four types of sludge for biosorption of cadmium in batch system. There were DWS (drinking water treatment plant sludge), LLS (landfill leachate sludge), ADSS (anaerobically digest sewage sludge) and SS (sewage sludge). The result indicated that SS had the most cadmium adsorption capacity of 0.38 mmol/g while DWS, LLS and ADSS were 0.13, 0.24 and 0.18 mmol/g, respectively. Moreover, cadmium adsorption was explained by Langmuir isotherm.

Razali et al. (2007) [49] presented the removal of different phosphorus compounds from aqueous solution by drinking water treatment sludge (DWTS). At pH 4.0 in batch system, the adsorption capacities of orthophosphate (KH_2PO_4), polyphosphate (($NaPO_3$)$_6$) and organic phosphate ($C_{10}H_{14}N_5O_7PH_2O$) were 0.2, 7.4 and 4.8 mg PO_4^{3-}/g DWTS, respectively. The adsorption behavior of different phosphorus species was fitted with Langmuir isotherm.

Hovsepyan et al. (2009) [50] demonstrated the adsorption of mercury using aluminium drinking water treatment residuals (Al-WTRs) as adsorbent. Al-WTRs had specific surface area of 48 m^2/g and internal micropore surface area of 120 m^2/g. In batch adsorption, Langmuir adsorption allowed to estimate the maximum mercury adsorption capacity of 79 mg Hg/g Al-WTRs. In addition, the adsorption kinetics fitted to a pseudo-first order. The mercury adsorption on Al-WTRs was efficient in the pH range of 3-8.

Oh et al. (2009) [51] studied the adsorption of hydrogen fluoride (HF) and fluoride ion (F^-) on water treatment sludge. In batch study, parameters affecting on total fluoride adsorption including pH, contact time, initial fluoride concentration and co-existing ions were investigated. The optimal adsorption of total fluoride was at pH 5.1 and the equilibrium time was of 48 hours. The adsorption fitted well Freundlich model. The value of K and 1/n in total fluoride adsorption were 4.396 and 0.822 (n=1.216), respectively. Furthermore, co-existing anions (SO_4^{2-}, NO_3^-, Cl^-) did not affect the efficiency of total fluoride adsorption onto the sludge.

Nagar et al. (2010) [52] presented Fe- and Al- based drinking water treatment residuals (WTR) as a low-cost alternative adsorbent for arsenate (As(V)). Fe-WTR showed a good adsorption closely 100% at the pH range of 3-7, whereas Al-WTR was a good adsorbent in the entire pH range. Moreover, the effect of competing ligands (phosphate and sulfate) and a complexing metal (calcium) were also studied.

Gibbons et al. (2011) [53] studied residual solids which collected from five water treatment productions in Canada. There are ferric, alum and lime water

treatment residuals (WTRs) for understanding removal of phosphate or arsenate adsorption on these residuals. Elemental analysis showed lime, ferric and alum residuals contain 7.04 mol Ca/kg solid, 4.86-4.96 mol Fe/kg solid and 3.62-4.67 mol Al/kg solid, respectively. Finally, ferric residual are the more efficiency adsorbent for phosphate or arsenate than lime and alum residual.

Hu et al. (2011) [54] removed glyphosate from aqueous environments by adsorption on alum industrial residual in dewater form (DAS) and liquid form (LAS). The maximum glyphosate adsorption capacity was calculated using Langmuir isotherm is 85.9 mg/g for DAS and 113.6 mg/g for LAS.

Kim et al. (2013) [55] studied the arsenite (As(III)) and arsenate (As(V)) adsorption using water purification sludge of facilities (Korea) in batch and column study. This research observed the effect of arsenic adsorption including pH of solution, initial arsenic concentration, contact time and competing anion. In addition, adsorption kinetic and adsorption isotherm at various temperatures were investigated. The result showed, the Langmuir isotherm was well fitted with arsenic adsorption. The maximum arsenite and arsenate adsorption at temperature 293 K were 8.89 and 5.13 mg As/g sludge, respectively. While, both of arsenite and arsenate adsorption kinetic were linearity in pseudo-second order.

As mentioned above, sludge residues from water treatment could be used in adsorption processes for various contaminants. Thus, this research focuses to recycle the sludge from the Metropolitan Waterworks Authority, Bangkhen, Bangkok, Thailand to be an alternative low-cost adsorbent for arsenite (As(V)), arsenate (As(V)) and dimethylarsenic acid (DMA) removal from wastewater in order to worthwhile utilize this solid waste.