CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of adsorbent

The sludge used in this research was obtained from the Metropolitan Waterworks Authority, Bangkhen, Thailand. It was dried in an oven for 24 hours at 105 °C. After that, the dried sludge was crushed and sieved through a 500 μm sieve. Its picture was shown in Figure 4.1. The color of the sludge powder was brown.

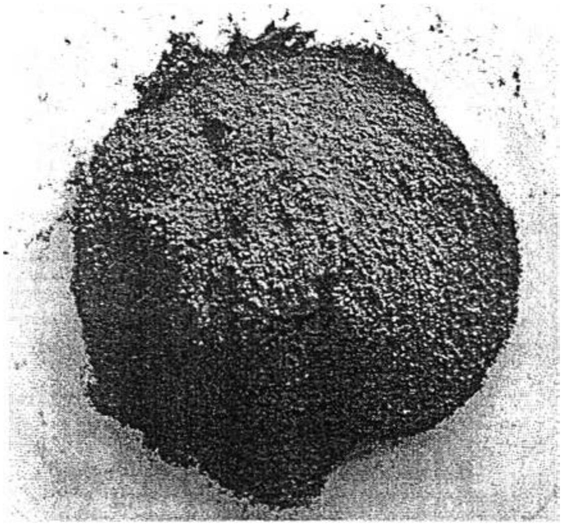

Figure 4.1 The sludge from the Metropolitan Waterworks Authority.

The characteristic physical properties of the sludge, such as surface area, total pore volume, average pore diameter were estimated by nitrogen adsorption analysis using BET technique. Furthermore, the elemental composition was investigated using XRF and ICP-OES. An XRD technique was also used for confirmation of the structure of compounds found in the sludge. All results were illustrated below.

4.1.1 Surface analysis

The BET isotherm was used for the determination of the surface property of sludge by nitrogen adsorption. The average surface area, total pore volume, average pore diameter of the sludge were summarized in Table 4.1.

Table 4.1 The result of surface analysis of the sludge

Sample	Surface area (m^2/g)	Total pore volume (cm^2/g)	Average pore diameter (nm)
Sludge from tap water production	43.44	0.2154	19.82

4.1.2 Elemental analysis (EA)

An CHNS/O analyzer was used for the determination of the contents of carbon, hydrogen and nitrogen in the sludge, the result was shown in Table 4.2.

Table 4.2 Amount of carbon, hydrogen and nitrogen in the sludge

Sample	%C	%H	%N
Sludge from tap water production	2.46	0.94	0.11

The elemental analysis (EA) result was used for the confirmation of the type of coagulant which was used during the treatment process of raw water. Since common coagulants used for removing impurities in raw water are classified in two types, inorganic and organic coagulants. If the percentages of carbon and hydrogen contents in the sludge are very high, coagulants employed in the process will be organic compounds. However, the result from Table 4.1 indicates the percentages of carbon and hydrogen is quite low, suggesting that the type of coagulant used was not organic compounds. Hence, we could imply that the type of coagulant used in the process at the Metropolitan Waterworks Authority mighty be inorganic compound. However, this implication shall be confirmed by other characterization techniques presented later on.

4.1.3 X-ray fluorescence spectrometer

XRF was used for demonstration of the elemental composition in the sludge. After that, the emission spectrum of elements in the sludge was investigated for elemental analysis. The XRF result was shown in Table 4.3

Table 4.3 X-ray fluorescence spectrometric result

Chemical composition of DWTS (%w/w)											
MgO	Al_2O_3	SiO_2	P_2O_5	CaO	TiO_2	MnO_2	Fe_2O_3	NiO	ZnO	ZrO_2	BaO
1.34	21.19	48.04	0.47	1.20	0.84	0.40	8.67	0.01	0.02	0.01	0.05

These XRF results suggested that the sludge contains high contents of Al, Fe and Si comparing with other elements as seen in Table 4.3. Consequently, the type of coagulant used for impurity removal from raw water was inorganic compound; such as alum ($Al_2(SO_4)_3.14H_2O$), poly aluminum chloride (PAC) and ferric salts ($FeCl_3$ $Fe_2(SO_4)_3$). In addition, raw water from the environment normally consists of high content of soil and sand. It is the case that the sludge residue has very high silica content. However, the standard metals for element analysis by XRF are pure metal standard; an interfering effect could be found in XRF measurement. From this reason, the amount of elements in the sludge calculated by XRF technique might be an error. Accordingly, the elemental analysis of the sludge using ICP-OES was required for confirmation of the amount of some metals as followed.

4.1.4 Inductively coupled plasma-optical emission spectrometry

Besides the elemental analysis by XRF technique, this research used ICP-OES for confirmation of the amount of elements in the sludge. The result was presented in Table 4.4.

The ICP-OES results confirmed that high contents of Al and Fe were found in the sludge at 113.8 and 43.7 mg/g, respectively while the sludge contained very low amount of As at 0.0195 mg/g. Nevertheless, this method cannot analyze the amount of Si in the sludge since SiO_2 is very difficult for digestion by the mixture of nitric acid and hydrochloric acid.

Table 4.4 The elemental analysis result by ICP-OES

Element	Chemical composition in sludge (mg/g)
Mg	4.8±0.3
Ca	6.3±0.5
Mn	1.69±0.05
Fe	43.7±3.5
Al	113.8±9.0

Both XRF and ICP-OES techniques confirmed that Al and Fe are the major elements in sludge because Al and Fe are naturally found in the suspended particles in raw water and in alum which is a source of Al was used as the coagulant in the water treatment process.

4.1.5 X-ray diffractometry (XRD)

XRD pattern of the sludge was shown in Figure 4.2.

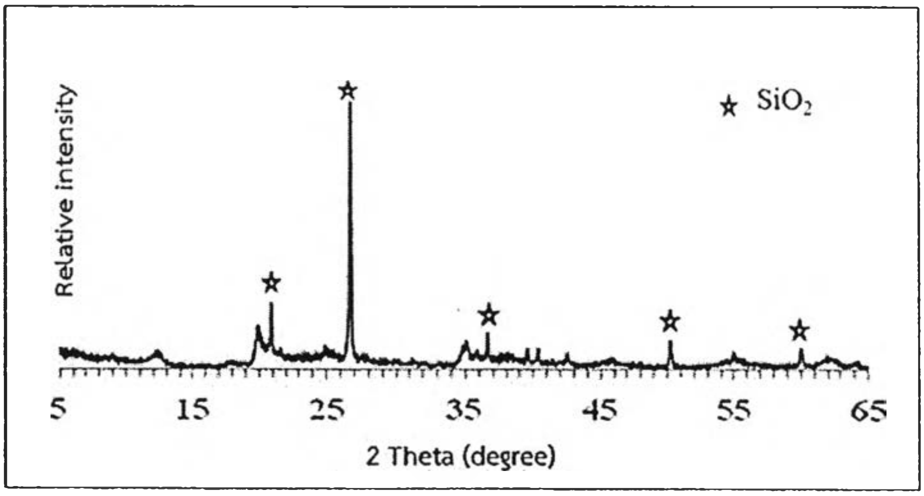

Figure 4.2 XRD diffractogram of the sludge.

The XRD result of the sludge showed the peak of crystalline form of SiO_2 that related to the pattern of quartz that is the most commonly found in nature of SiO_2. While, any peak of crystalline form of Al and Fe hydroxides was not observed in the XRD investigation (Figure 4.1). Therefore, Al and Fe hydroxides might be amorphous structures.

4.1.6 Point of zero charge

Since the mechanism responsible for arsenic adsorption onto sludge is difficult to understand due to the fact that the surface functional group cannot be well identified. Thus, the study of pH of point of zero charge (pH_{pzc}) could be useful to explain arsenic adsorption mechanism since it might play a crucial factor in arsenic adsorption process on sludge. In the past, several researchers have used pH_{pzc} for determination of metal sorption onto natural or waste materials [57].

At pH_{pzc}, the positive charge on surface site of sorbent is equal to the negative charge as sorbent surface net charge takes a zero. Moreover, the hypothesis of pH_{pzc} study includes;

- At pH of solution > pH_{pzc}, sorbent surface is negatively charged and could interact with positive metal species
- At pH of solution < pH_{pzc}, solid surface is positively charged and could interact with negative species.

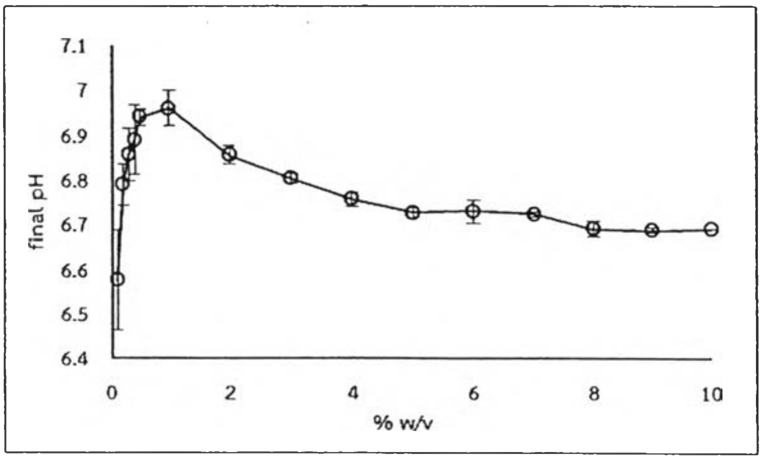

Figure 4.3 Mass titration curve for the determination of pH_{pzc} of the sludge.

This research used the mass titration method for determination of pH_{pzc} of the sludge. The result indicated that pH_{pzc} of sludge is approximately 6.7 as shown in Figure 4.3.

4.2 Adsorption study by batch method

In batch method, the sludge was used as adsorbent in adsorption study of arsenite (As(III)), arsenate (As(V)) and dimethylarsenic acid (DMA) in aqueous solution at room temperature. The effects of pH solution, contact time and initial arsenic concentration were investigated to acquire the optimal conditions for arsenic removal and the adsorption isotherm study was also elucidated.

The efficiency of arsenic adsorption was illustrated in terms of percent removal and adsorption amount, q (mg/g) which were calculated according to Equation 4.1 and Equation 4.2, respectively.

$$\text{Arsenic removal (\%)} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \qquad (4.1)$$

$$\text{Adsorption amount } (q) = \frac{(C_i - C_e)V}{m} \qquad (4.2)$$

where C_i = initial concentration of arsenic in aqueous solution (mg/L)

C_e = equilibrium concentration of arsenic in aqueous solution (mg/L)

q = adsorption amount (mg/g)

V = volume of aqueous solution (mL)

m = mass of adsorbent (g)

4.2.1 Effect of pH of arsenic solution

The pH is a crucial factor which affects the efficiency of arsenic adsorption due to arsenic species change upon the change of pH as mentioned in Section 2.1.2 [18]. The experiments were performed using 10 mg/L of arsenic solution. The pH was adjusted by HCl and/or NaOH solution in pH range of 1-10. Arsenic solution (10 mL) was added into 0.05 g of sludge in a test tube and shaken for 24 hours at room temperature. Then, residual arsenic in solution was determined by ICP-OES. The result of effect of arsenic solution was shown in Figure 4.4.

From Figure 4.4, the sludge showed the highest adsorption efficiency for As(V) when compared with As(III) and DMA. At pH 2, the percent removal of As(V), As(III) and DMA were 97.5, 24.9 and 34.7 %, respectively. Nevertheless, the As(V) adsorption efficiency on the sludge sorbent decreased as the pH of solution increased. Since As(V) in water exits as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (pKa_1 = 2.3, pKa_2=6.9 and pKa_3 = 11.5), at low pH, As(V) mainly occurs in $H_2AsO_4^-$ form. And at the pH of solution < pH_{pzc} of sludge sorbent (6.7), the surface of sludge sorbent is positively charged. Therefore, the negatively charged $H_2AsO_4^-$,) could be adsorbed strongly on the positively charged surface of sludge. Thus, the sludge shows the highest efficiency for As(V) adsorption at the pH around 2.

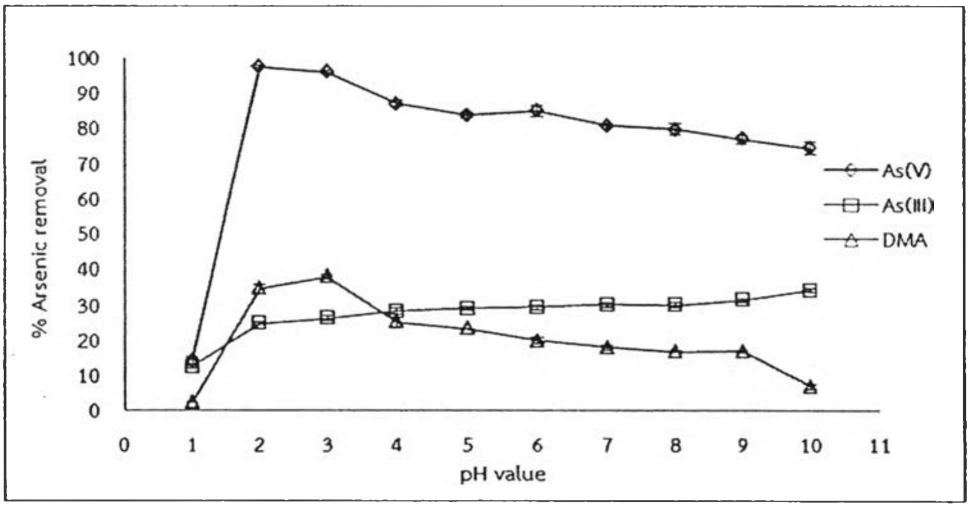

Figure 4.4 Effect of pH on As(III), As(V) and DMA adsorption (initial concentration = 10 mg/L,V = 10 mL, adsorption time = 24 h and adsorbent = 0.05 g).

For As(III), it was found as H_3AsO_4, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-} (pKa_1 = 9.2, pKa_2 = 12.1, pKa_3 = 12.7). As(III) normally occurs in neutral forms at low pH whereas the negatively charged forms of As(III) can be found in the pH of solution > 9.2 that the charge on sludge surface is negative at high pH value. The repulsion between negatively charged As(III) species and negatively charged sludge sorbent might be occurred. Additionally, the sludge sorbent provided the highest percent removal of As(III) at around 34% at pH 10. As the result, this sludge showed that the efficiency of As(III) adsorption was not good.

Like As(III), DMA was found as $(CH_3)_2As(O)(OH)$ and $(CH_3)_2As(O)O^-$ (pKa_1 = 6.2) [3]. DMA is mainly presented in a neutral form at pH < 6.2, whereas the negatively charged form can be found in the pH of solution over 6.2. The graph showed the highest percent removal of DMA at around 38% at pH 3.

From the study of effect of solution pH, it indicated that the highest percent removal of As(V), As(III) and DMA adsorption on the sludge sorbent occurred at different pH value. However, total arsenic removal from water is a topic of interest pH 2 was considered as optimal pH for further adsorption study due to the highest adsorption amount of total arsenic (the sum of As(V), As(III) and DMA adsorption amounts).

4.2.2 Effect of contact time

Contact time is one of important parameters that several researchers have to concern for studying the metal adsorption in batch system.

The effect of contact time for arsenic adsorption on the sludge sorbent was studied using arsenic solution at pH 2 which was the optimal pH from previous experiment. Then, 10 mL of 10 mg/L As(V), As(III) and DMA was added to 0.05 g of sludge in a test tube and shaken at different times ranging from 0.5-24 hours at room temperature. The result of the effect of contact time on each adsorption of As(V), As(III) and DMA as a function of time is shown in Figure 4.5. From the graphs, contact equilibrium time of As(V), As(III) and DMA were obtained after 720 minutes or 12 hours.

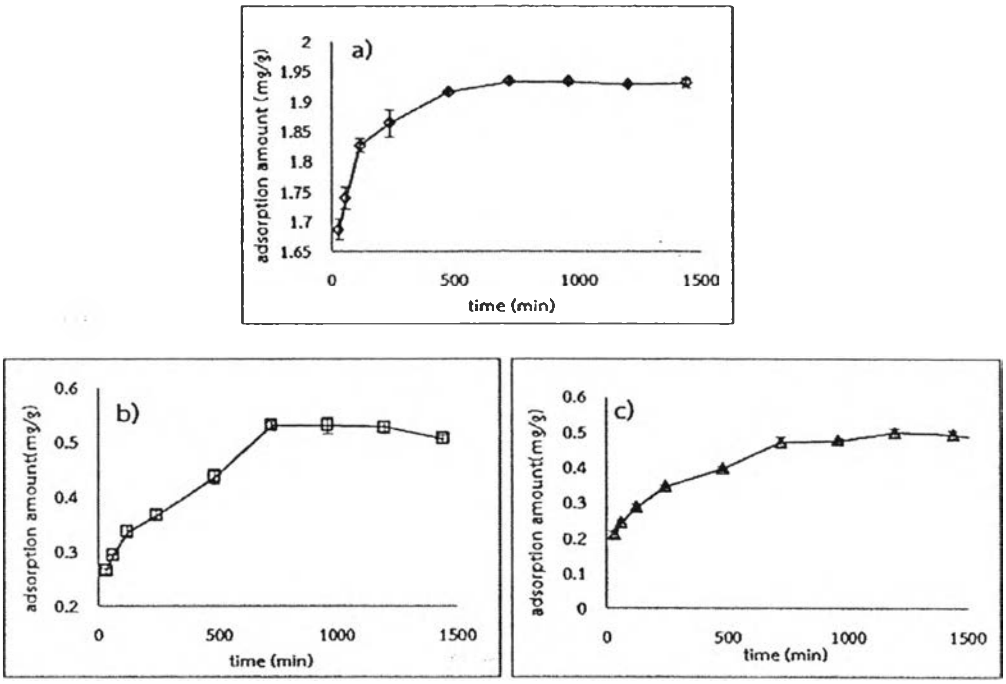

Figure 4.5 Effect of contact time on adsorption of a) As(V), b) As(III) and c) DMA at various times. (initial concentration = 10 mg/L, V = 10 mL, pH = 2 and adsorbent = 0.05 g).

4.2.3 Adsorption kinetics

The adsorption kinetics of each adsorption of As(V), As(III) and DMA on the sorbent were investigated using the pseudo-first order equation proposed by Lagergren [28] and the pseudo-second order kinetic model proposed by McKay [58]. The kinetics used to understand the residence time of a sorbate uptake rate at the sorbent-solution interface. It is a crucial parameter for predicting the time for arsenic removal in treatment plants. Consequently, the linear form of pseudo-first order is expressed according Equation 4.3 while a pseudo-second order is given following Equations 4.4. In addition, the derived equation of linearized pseudo-second order is presented following Equation 4.6. Then, h value can be estimated using Equation 4.5.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{4.3}$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4.4}$$

$$h = k_2 {q_e}^2 \tag{4.5}$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \tag{4.6}$$

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

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

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

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

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

The characteristics of pseudo-first order and pseudo-second order kinetics of the adsorption of As(V), As(III) and DMA on the sludge sorbent were shown in Figure 4.6 and 4.7, respectively. The prediction of a model best-fitted to each arsenic adsorption on the sorbent was based on the correlation coefficient (R^2, value close or equal to 1) by comparison of the R^2 that was acquired from the pseudo-first order and the pseudo-second order equations.

The result demonstrated that the correlation coefficient (R^2) was close to 1 for the pseudo-second order kinetics model than the pseudo-first order kinetics model. These results indicated that the studied adsorption process showed a good compliance with the proposed pseudo-second order kinetics model. Additionally, the literature explained that the pseudo-second order kinetics includes different adsorptions such as surface complexation, ion exchange. Moreover, the assumption of pseudo-second order model is based on the rate-limiting step that may be chemisorption involving valent force through an exchange of electron between sorbent sites and sorbate molecules [59].

Several parameters of pseudo-first order kinetics model and pseudo-first order kinetics model were summarized in Table 4.5 and 4.6, respectively.

From the result, the experimental adsorption capacities ($q_{e(exp)}$) at equilibrium of As(V), As(III) and DMA were 1.93, 0.53 and 0.47 mg/g. respectively. These values are very close to the adsorption amounts at equilibrium of As(V), As(III) and DMA from the calculation ($q_{e(cal)}$) of pseudo-second order equation that were 1.93, 0.46 and 0.51 mg/g, while $q_{e(cal)}$ of As(V), As(III) and DMA from the pseudo-first order were 0.26, 1.00 and 0.26 mg/g, respectively. This result confirmed that the pseudo-second order kinetics model is more valid.

Table 4.5 Pseudo-first order kinetics constant for adsorption of arsenic on sludge sorbent

As	Equation	R^2	k_1 (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)
As(V)	Y = -0.0025x – 0.5854	0.9860	0.0058	1.93	0.26
As(III)	Y = -0.001x – 0.5648	0.9887	0.0023	0.53	1.00
DMA	Y = -0.0012x – 0.5769	0.9840	0.0005	0.47	0.26

Table 4.6 Pseudo-second order kinetics constant for adsorption of arsenic on sludge sorbent

As	Equation	R^2	k_1 (min^{-1})	$q_{e(exp)}$ (mg/g)	$q_{e(cal)}$ (mg/g)	h (mg g^{-1} min^{-1})
As(V)	Y = 0.5166x + 3.3885	0.9999	0.0788	1.93	1.94	0.30
As(III)	Y = 2.1729x + 80.717	0.9927	0.0585	0.53	0.46	0.01
DMA	Y = 2.3361x + 107.82	0.9957	0.0242	0.47	0.51	0.01

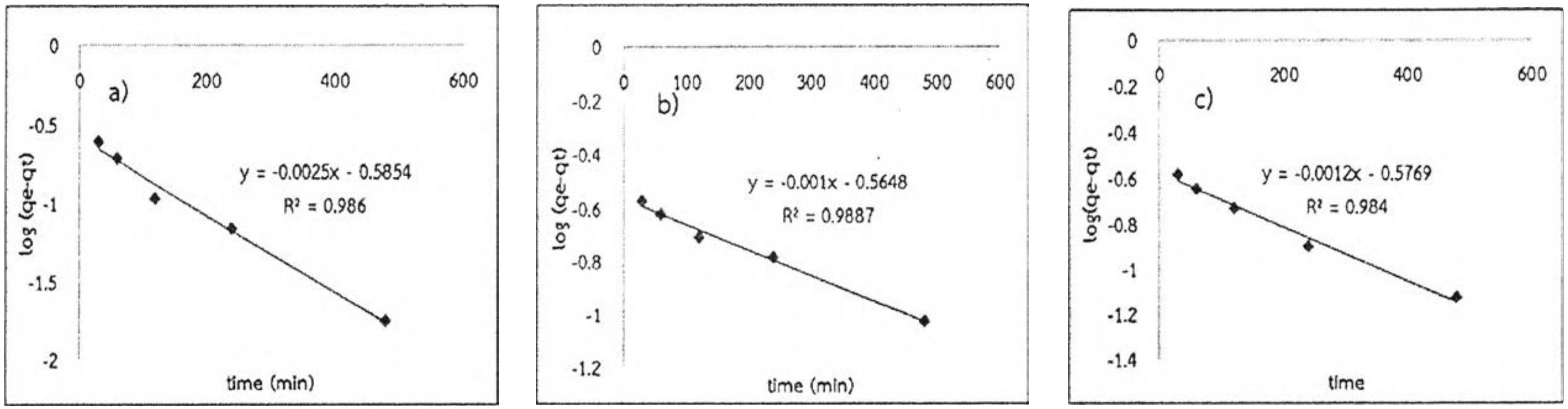

Figure 4.6 Pseudo-first order kinetics plots of arsenic adsorption on sludge sorbent a) As(V) b) As(III) and c) DMA (initial concentration = 10 mg/L, V = 10 mL, pH = 2 and adsorbent = 0.05 g and t = 12 h).

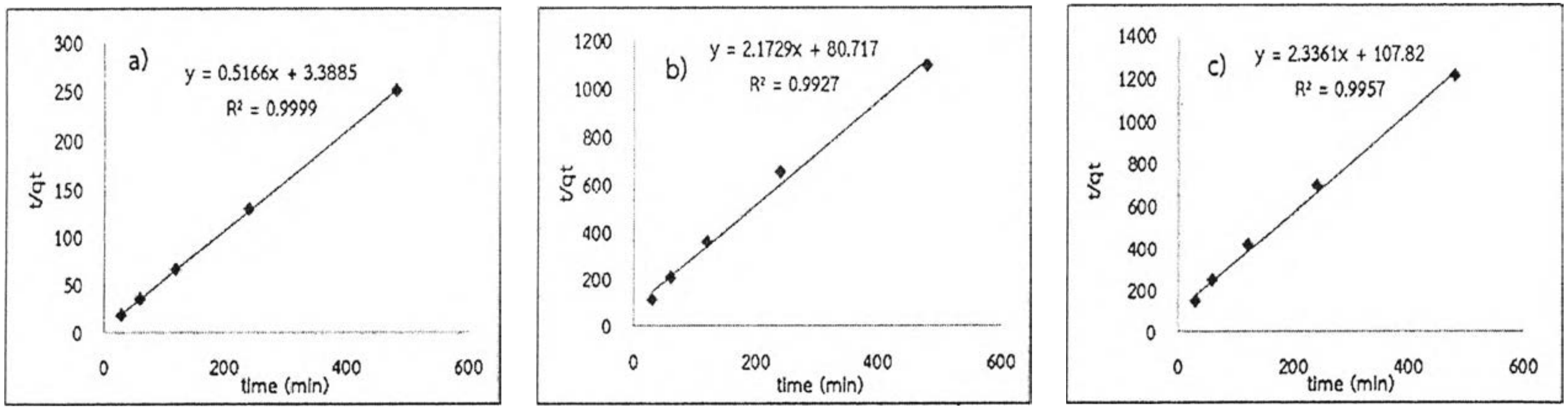

Figure 4.7 Psedo-second order kinetics plots of arsenic adsorption on sludge sorbent a) As(V) b) As(III) and c) DMA (initial concentration = 10 mg/L, V = 10 mL, pH = 2 and adsorbent = 0.05 g and t = 12 h).

4.2.4 Effect of initial arsenic concentration and adsorption isotherms

The effect of initial arsenic concentration was elucidated using optimal conditions from the previous experiment. Arsenic solution (10 mL) in various concentrations of 1 to 100 mg/g at pH 2 were added to 0.05 g of sludge in a test tube and shaken at room temperature for 12 hours. After that, the remaining arsenic in solution at equilibrium time was analyzed by ICP-OES.

The relationship between the adsorption amount (mg/g) and the remaining analyte concentration in solution at room temperature is called an "adsorption isotherm" which was presented in Figure 4.8. It presents the information for discussing the phenomenon of adsorption. The commonly used mathematic models were the Langmuir and Freundlich models.

Firstly, the Langmuir adsorption isotherm is a model for a description of sorption phenomena and applied to adsorption on completely homogeneous surface with presumably negligible interaction between adsorbed molecules. In addition, this adsorption is a reversible process which the form of Langmuir isotherm is represented in Equation 4.7.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{4.7}$$

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

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

q_m = the maximum adsorption amount (mg/g)

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

Next, the Freundlich adsorption isotherm is developed from the Langmuir isotherm. The Freundlich model is used for assuming the adsorption of sorbates on multilayer surface of adsorbent. This isotherm is presented by the following Equation 4.8.

The experiment data of initial arsenic concentration were taken for linear plotting using the Langmuir and Freundlich equations that were shown in Figure 4.9 and 4.10. Moreover, their adsorption isotherm parameters were calculated and listed in Table 4.7 and 4.8.

$$\log q = \log K_f + \frac{1}{n}\log C_e \qquad (4.8)$$

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

n = Freundlich constant related to adsorption intensity

Base on the correlation coefficient, the result suggested that the characteristic of As(V) adsorption on the sludge sorbent was more accurately fitted to the Langmuir model (R^2 = 0.9929) than the Freundlich model (R^2 = 0.9469). The maximum adsorption amount (q_m) and the constant related to the free energy (b) of As(V) adsorption from the Langmuir equation were 9.01 mg/g and 0.3986 L/mg, respectively. Furthermore, the maximum adsorption from the Langmuir isotherm meant that only a monolayer adsorption is formed. The b value indicated that arsenate has a stronger binding affinity onto the sludge sorbent.

For As(III) and DMA adsorption, they were better fitted to the Freundlich isotherm (R^2 = 0.9775-0.9936) than the Langmuir isotherm (R^2 = 0.9351-0.9572) suggesting that the adsorption of As(III) and DMA likely occurs on a heterogeneous surface.

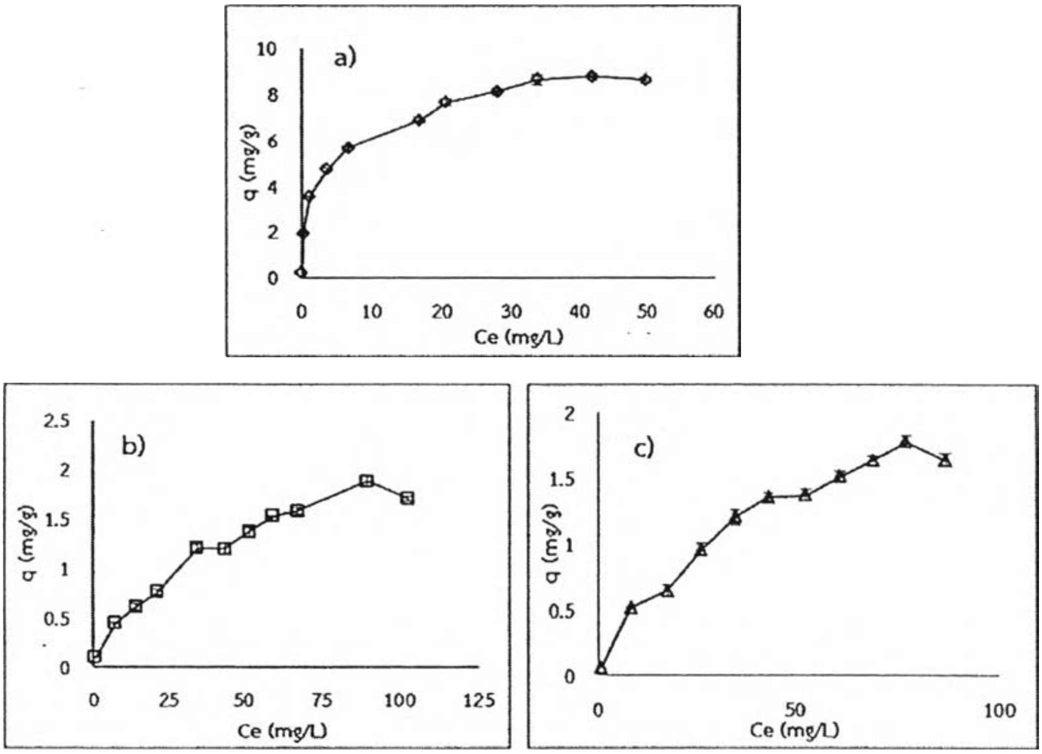

Figure 4.8 The relation between arsenic concentration at equilibrium and adsorption amount for a) As(V), b) As(III) and c) DMA (initial concentrations = 1-100 mg/L, V = 10 mL, time= 12 h, pH = 2, and adsorbent weight = 0.05 g).

Nevertheless, the correlation coefficients (R^2) of As(V), As(III) and DMA in Table 4.7 and 4.8 were close to 1 in both Langmuir and Freundlich equations. The adsorption of As(V), As(III) and DMA fitted to both models. Therefore, the reporting of maximum adsorption amount (q_m) of As(V), As(III) and DMA in this research was based on the value from the Langmuir equation ($q_{m(cal)}$) which were 9.00, 2.29 and 2.44 mg/g, respectively.

As the maximum As(V) adsorption amount on the sludge in this research was calculated from the Langmuir isotherm, the As(V) adsorption amount of many low cost materials were also concluded for the comparison with this sludge, some of which were given in Table 4.9.

Table 4.7 Parameters of the Langmuir isotherm for adsorption of arsenic

As	Equation	R^2	$q_{m(exp)}$ (mg/g)	$q_{m(cal)}$ (mg/g)	b (L/mg)
As(V)	Y = 0.111x + 0.2785	0.9929	8.76	9.01	0.40
As(III)	Y = 0.4359x +13.643	0.9351	1.88	2.29	0.03
DMA	Y = 0.4106x + 15.212	0.9572	1.78	2.44	0.03

Table 4.8 Parameters of the Freundlich isotherm for adsorption of arsenic

As	Equation	R^2	K_f (mg/g)	n
As(V)	Y = 0.4508x + 0.355	0.9469	2.26	2.46
As(III)	Y = 0.5780x - 0.8631	0.9936	0.99	1.73
DMA	Y = 0.7082x + 1.0675	0.9775	0.98	1.41

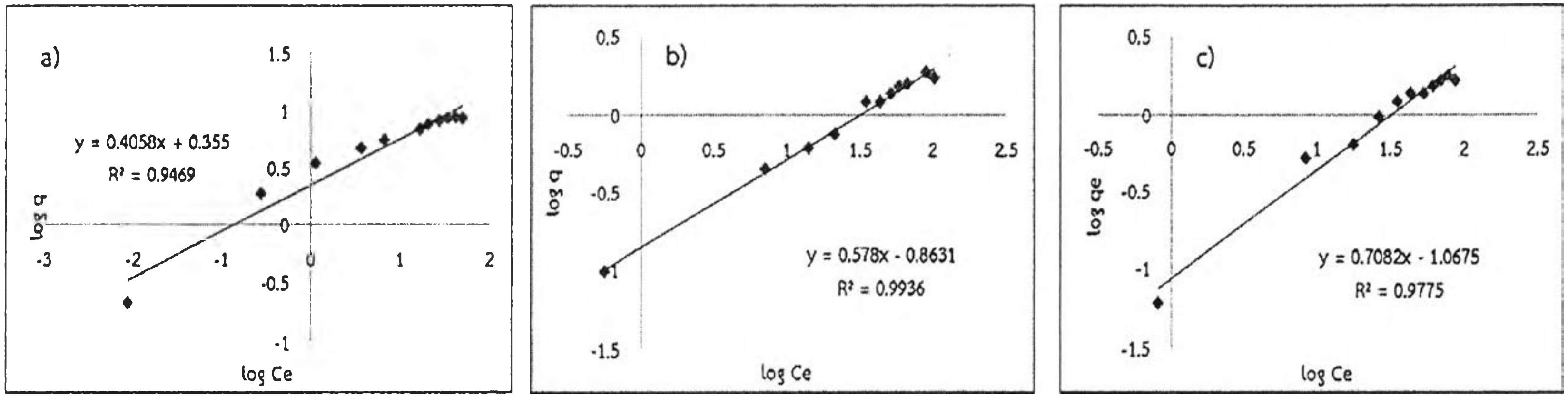

Figure 4.9 Langmuir isotherm plots of a) As(V) b) As(III) and c) DMA. (initial concentration = 1-100 mg/L, V = 10 mL, time = 12 h, pH = 2, and adsorbent = 0.05 g).

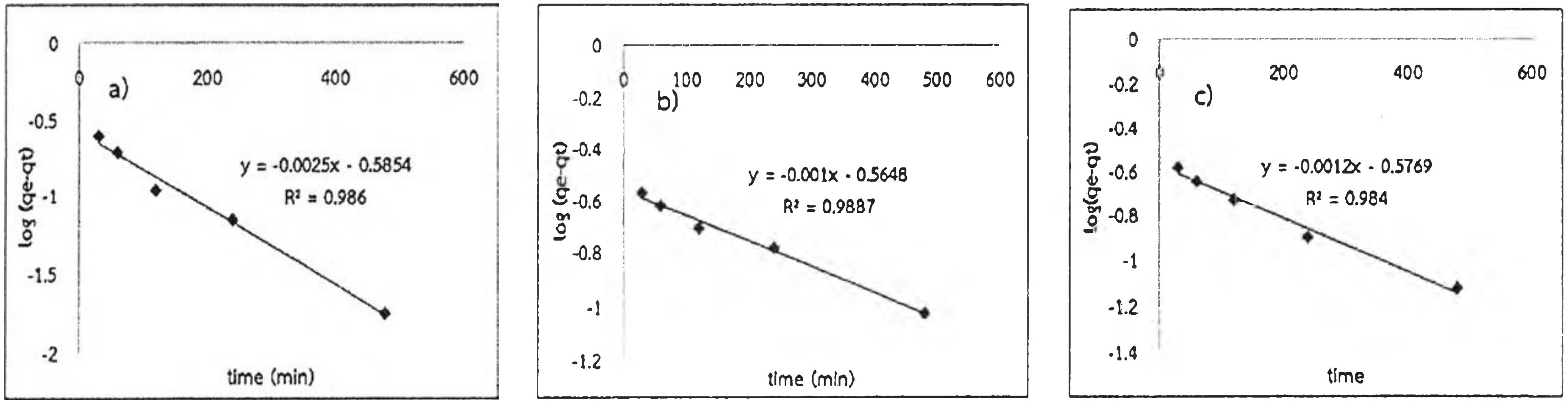

Figure 4.10 Freundlich isotherm plots of a) As(V) b) As(III) and c) DMA. (initial concentration = 1-100 mg/L, V = 10 mL, time = 12 h, pH = 2, and adsorbent = 0.05 g).

Table 4.9 Adsorption amounts of some adsorbent for As(V) adsorption

Type of adsorbent	Adsorption amount (mg/g) of As(V)	Reference
Sludge from tap water production	9.01	This research
Industrial solid waste	11.02	[40]
Red mud	6.86	[41]
Tropical soil	0.22	[42]
Waste ash	5.37	[43]
Solid waste from leather industry	26.00	[44]
Natural laterite	0.565	[45]
Water purification sludge	5.13	[55]

4.2.5 Effect of competing ions

Phosphate and sulphate were tested for studying the effect of competing ions since both PO_4^{3-} and SO_4^{2-} have a similar oxyanion structure to that of arsenic. Moreover, many arsenic adsorption researches have normally studied the effect of co-existing anions using PO_4^{3-} and SO_4^{2-} [52, 55]. Thus, this experiment used PO_4^{3-} and SO_4^{2-} at various mole ratios to arsenic of 1:1, 5:1, 10:1 and 20:1. The result was shown in Figure 4.11.

From Figure 4.11, the efficiency of adsorption of As(V), As(III) and DMA on the sludge sorbent decreased with increasing the mole ratio of phosphate to arsenic, suggesting that phosphate has significant effect on arsenic adsorption due to the fact that phosphate has tetrahedral structure similar to arsenate and the charge of phosphate (-3) also has more negatively than sulphate (-2), whereas sulphate did not interfere the arsenic adsorption. Furthermore, phosphorous (P) is in the same group VA in the periodic table of the elements like arsenic (As) resulting that some properties of phosphorous compounds are similar to arsenic.

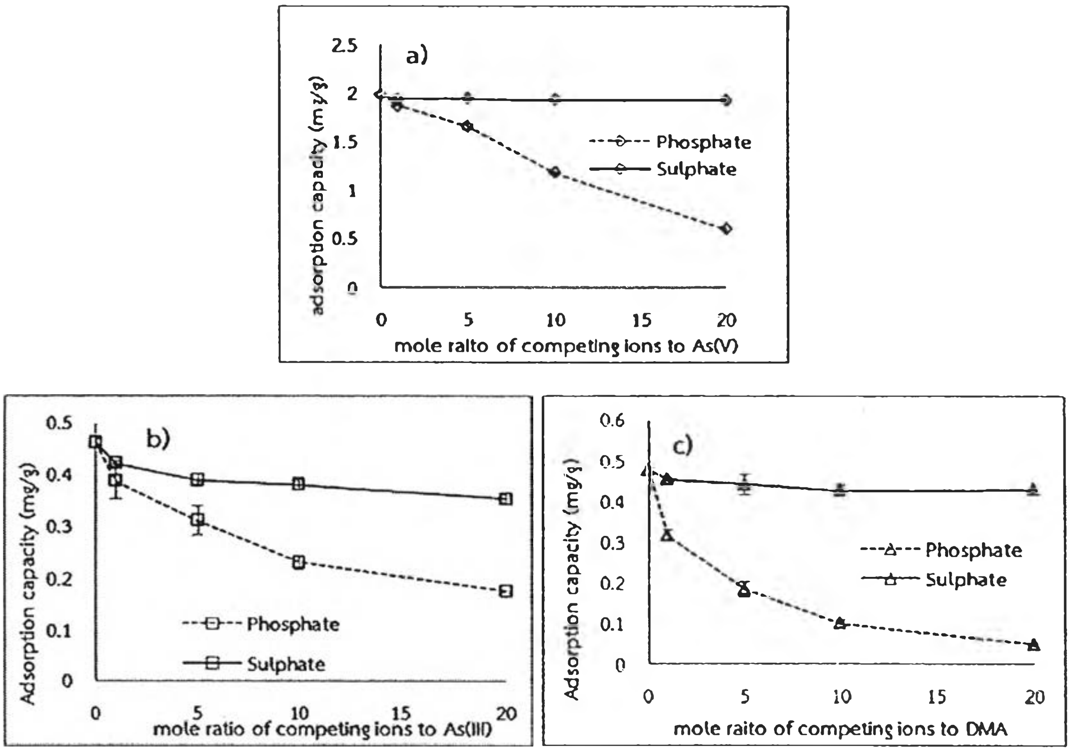

Figure 4.11 Effect of competing ions with various mole ratios of a) As(V) b) As(III) and c) DMA (initial concentration = 10 mg/L, V = 10 mL, time = 12 h, pH = 2, and adsorbent = 0.05 g).

4.3 Adsorption study by column system

Based on the previous observation, the sludge sorbent has an exceptional performance for arsenic removal in a batch system. However, arsenic adsorption in batch type has limitation for a large volume of arsenic solution, while a column system has an advantage over this limitation due to the fact that arsenic can be continuously adsorb to a given quantity of fresh sludge sorbent. Furthermore, the treatment plants commonly employed a column system for pollutants removal from water. Therefore, this research interested to study the efficiency of arsenic removal by column method that various parameters influencing arsenic adsorption were studied using a homemade cylinder column. The column system for arsenic removal was operated following Figure 4.12.

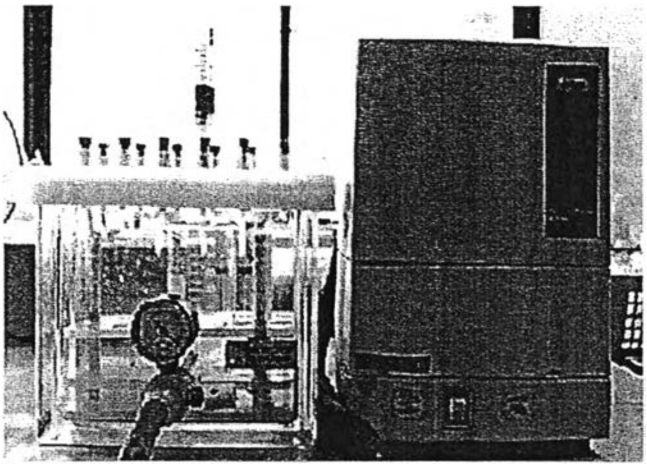

Figure 4.12 Photograph of column system for arsenic removal.

4.3.1 Effect of flow rate

In the column method, a homemade cylinder column was packed with the sludge sorbent at a height of 1 cm (0.89 g sludge). The flow rates of arsenic solution were investigated at 0.5, 1, 2, 3 and 4 mL/min using 25 mL of 10 mg/L each arsenic solution. This experiment was performed in triplicate. The result was shown in Tables 4.10, 4.11 and 4.12 and Figures 4.13.

Table 4.10 Effect of flow rate of As(V) adsorption on sludge sorbent

column height	weigh of sludge	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
1 cm	0.89	0.5	1.9545 ± 0.0002	99.58 ± 0.01
		1	1.9539 ± 0.0001	99.56 ± 0.01
		2	1.88 ± 0.09	97.09 ± 4.84
		3	1.9408 ± 0.0006	99.69 ± 0.03
		4	1.9410 ± 0.0003	99.70 ± 0.01

Table 4.11 Effect of flow rate of As(III) adsorption on sludge sorbent

column height	weigh of sludge	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
1 cm	0.89	0.5	0.79 ± 0.06	40.63 ± 3.17
		1	0.74 ± 0.03	38.10 ± 1.69
		2	0.61 ± 0.06	31.38 ± 3.20
		3	0.48 ± 0.03	24.90 ± 1.65
		4	0.48 ± 0.06	24.95 ±2.98

Table 4.12 Effect of flow rate of DMA adsorption on sludge sorbent

column height	weigh of sludge	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
1 cm	0.89	0.5	1.18 ± 0.08	61.30 ± 4.36
		1	1.23 ± 0.04	60.33 ± 1.99
		2	1.01 ± 0.05	52.52 ± 2.67
		3	0.77 ± 0.04	40.25 ± 2.36
		4	0.77 ± 0.04	40.34 ± 1.92

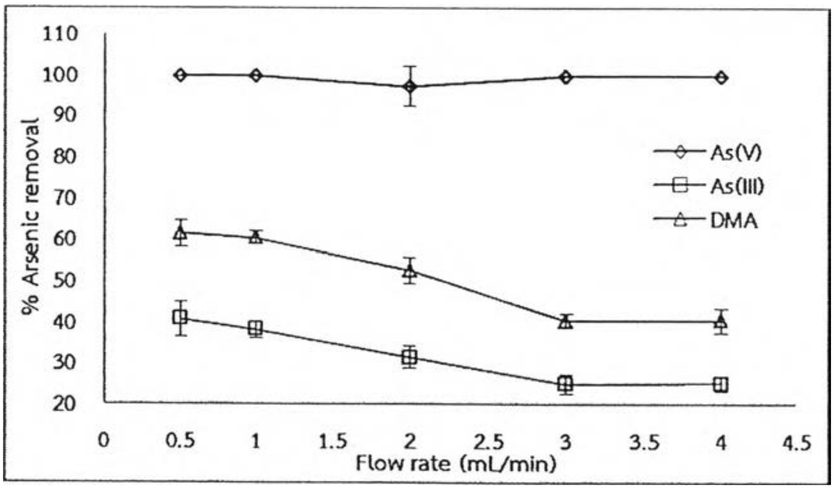

Figure 4.13 Relation between flow rate and the percent removal of As(V), As(III) and DMA at the adsorbent layer height at 1 cm.

From the result, the percent removal of As(V) in column study at various flow rates of solution of 0.5-4 mL/min were in the same order of efficiency (97-99%), while the ability of As(III) and DMA removal decreased at the flow rate 2 and 4 mL/min. Because the adsorption process of arsenic onto the sorbent surface may not be complete at high flow rates. At the solution flow rate of 0.5 mL/min, the percent removal of As(III) and DMA showed the highest percentage at 40.63 and 61.30%, respectively.

The proper flow rate for studying the effect of column height was chosen at 1 mL/min because the percent removal of As(III) and DMA at 0.5 mL/min and 1 mL/min were close. In addition, the low flow rate of 0.5 mL/min was not suitable due to a lot time required for passing the solution through the column. Hence, the optimal flow rate of arsenic solution was chosen at 1 mL/min.

4.3.2 Effect of adsorbent layer height

The sludge adsorbent was packed into cylindrical columns, each having different absorbent layer heights (1.0, 1.5, and 2.0 cm). This experiment was performed in triplicate. The result was shown in Table 4.13, 4.14 and 4.15 and Figure 4.14.

The result indicated that the column height significantly affected the arsenic adsorption. As the absorbent layer height related to the amount of sludge sorbent, the adsorbent bed height at 2 cm showed the percent removal of As(III) and DMA which were approximately of 73 and 90%, respectively. Due to an increase in the amount sludge sorbent, the adsorptive surface sites for arsenic also increased. For As(V) removal, the percent removal of As(V) was close to 100% at all adsorbent bed height because this sludge sorbent possessed a very good efficiency for As(V) removal as mentioned in the batch system. Therefore, the optimal flow rate and adsorbent bed height for arsenic removal in the column system were 1 mL/min and 2 cm, respectively. This condition was used for the investigation of breakthrough curve.

Table 4.13 Effect of column height of As(V) adsorption on sludge sorbent

column height (cm)	weight of sludge (g)	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
0.5	0.55	1	1.94 ± 0.02	98.80 ± 1.25
1	0.89	1	1.9539 ± 0.0001	99.55 ± 0.01
1.5	1.45	1	1.9545 ± 0.0002	99.58 ± 0.01
2	1.88	1	1.9932 ± 0.0007	99.84 ± 0.04

Table 4.14 Effect of adsorbent layer height of As(III) adsorption on sludge sorbent

column height (cm)	weight of sludge (g)	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
0.5	0.55	1	0.37 ± 0.03	18.84 ± 1.61
1	0.89	1	0.76 ± 0.06	38.44 ± 3.06
1.5	1.45	1	1.20 ± 0.06	62.53 ± 3.23
2	1.88	1	1.45 ±0.11	73.29 ± 5.69

Table 4.15 Effect of column height of DMA adsorption on sludge sorbent

column height (cm)	weight of sludge (g)	flow rate (mL/min)	adsorption amount (mg/g)	% arsenic removal
0.5	0.55	1	0.69 ± 0.10	33.56 ± 4.72
1	0.89	1	1.24 ± 0.04	60.33 ± 1.99
1.5	1.45	1	1.65 ± 0.03	80.33 ± 1.63
2	1.88	1	1.80 ± 0.04	89.69 ± 2.13

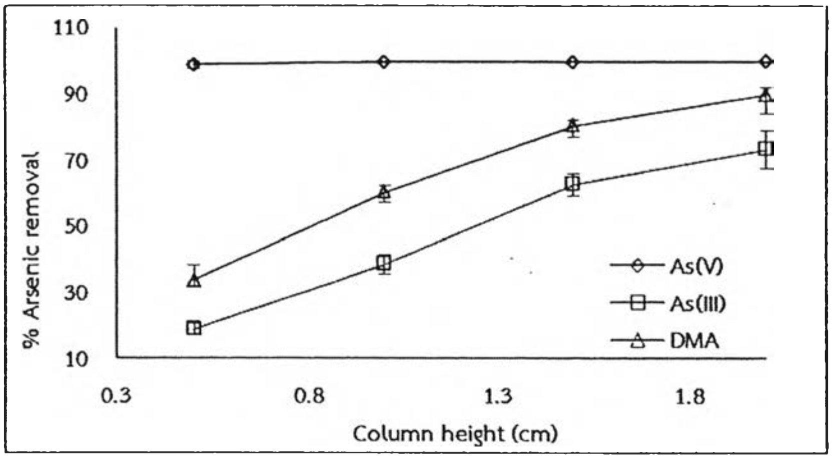

Figure 4.14 The relation between the adsorbent layer height and the percent removal of As(V), As(III) and DMA (at flow rate 1 mL/min).

4.3.3 Breakthrough curve

A breakthrough study was carried out for determination of the adsorption capacity of arsenic on a homemade mini column packed with sludge sorbent at column height 2 cm of 1.88 g of sludge. A plot of ratio of the remaining arsenic in solution (C_i) versus the initial arsenic concentration (C_0) for determination breakthrough curve was illustrated in Figure 4.15.

Figure 4.15 demonstrated the completion of As(V) adsorption on the sludge in the first eight sequences (up to 200 mL of sample volume) in which the value of C_i/C_0 is around zero. Then, the ratio C_i/C_0 of As(V) increased roughly to 0.99 that the column completely exhausted to adsorb As(V) on the sludge at 725 mL of sample volume. For As(III) and DMA, their adsorption was not complete at the first sequence of sample indicated by the ratio C_i/C_0 of 0.39 and 0.27, respectively. In addition, the maximum adsorption capacity of As(V), As(III) and DMA calculated from the breakthrough curves were of 2.42, 1.70 and 1.36 mg/g, respectively.

After all, a raito C_i/C_0 of As(V) at 0.05 was used as a breakthrough point and the integrated area of the breakthrough curve below this ratio was calculated for determination of the quantity of As(V) retaining in the solution. However, this calculation cannot be applied for As(III) and DMA adsorption since their incomplete adsorption was found at the beginning of investigation.

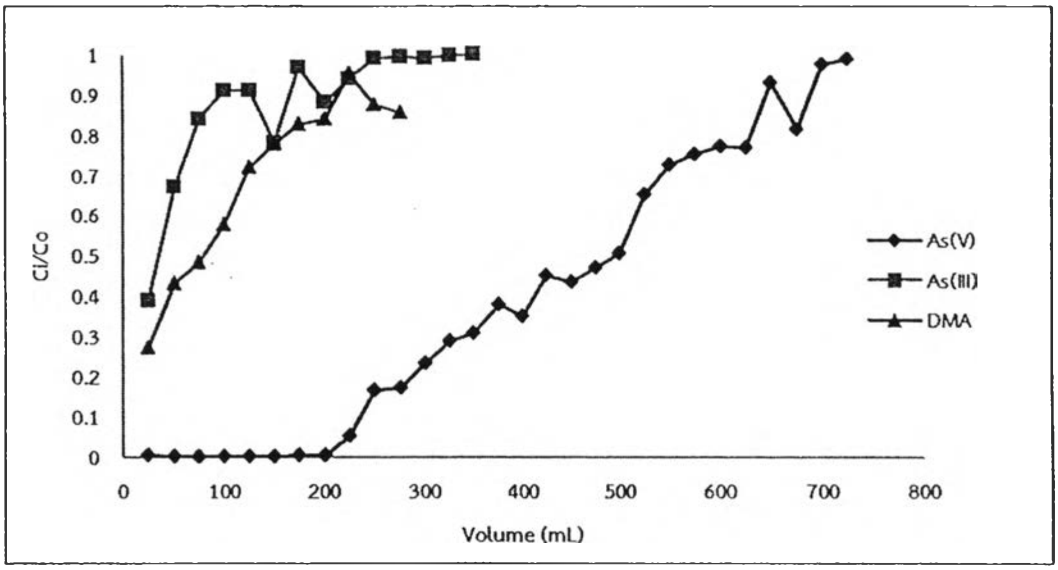

Figure 4.15 Breakthrough curves of arsenic adsorption on column system.

4.4 Application in real contaminated water samples

Two wastewater samples were obtained from the petroleum industry and subject to total arsenic removal in batch and column systems. There are TK80 and TK81 samples. Additionally, arsenic-spiked surface water samples were used in this aspect.

4.4.1 Arsenic removal from contaminated water samples

The adsorption amount and percent removal of total arsenic in wastewater using batch system were summarized in Table 4.16. The result showed that the percent removal of arsenic for TK80 and TK81 were 17.58 and 11.21%, respectively. At these low percentages, the efficiency of arsenic removal from real samples using batch system seemed unsatisfactory. Due to high arsenic concentration level in real wastewater samples around 74-77 mg/L, the amount of sludge sorbent was not sufficient. Thus, this method can be improved by increasing the amount of sludge sorbent. In addition, these wastewaters are composed of As(III) and DMA in high concentration (data not published due to the confidentiality of the samples provider), whereas this sludge sorbent have good efficiency for As(V). These might be the main cause that the percent removal of total arsenic in real wastewaters was not high.

Table 4.16 The result of arsenic removal in wastewater using batch system

real wastewater	initial arsenic concentration (mg/L)	adsorption amount (mg/g)	% arsenic removal
TK80	74.60	2.62 ± 0.04	17.58 ± 0.25
TK81	77.11	1.73 ± 0.02	11.21 ± 0.14

Table 4.17 The result of arsenic removal in wastewater using column system

real wastewater	initial arsenic concentration (mg/L)	adsorption amount (mg/g)	% arsenic removal
TK80	74.60	5.85 ± 0.88	39.21 ± 5.90
TK81	77.11	5.30 ± 0.37	34.37 ± 2.39

For the column system, the adsorption capacity and percent removal were presented in Table 4.17. The result showed that the percent removal for TK80 and TK81 were 39.21 and 34.37%, respectively. This result suggested that the column system can apply for the removal arsenic from wastewater. However, the drawback of arsenic removal using column system is the column clogging during the operation possibly caused by the breaking of sludge sorbent into very tiny particles after a long time immersion in the solution.

4.4.2 Arsenic removal from surface water sample

Arsenate (As(V)) was spiked into a water sample collected from the pond of Chulalongkorn University to obtain a final arsenic concentration of 10 mg/L. The removal was performed in both batch and column systems. The result was concluded in Table 4.18.

The result suggested that the percent removal of arsenate (As(V)) was nearly 100%. It confirmed that the sludge from Metropolitan Waterworks Authority has potential for As(V) removal from natural water.

Table 4.18 The result of arsenic removal from natural water sample using batch and column systems

water sample		adsorption method	adsorption amount (mg/g)	% arsenic removal
before spiked (mg/L)	after spiked (mg/L)			
n.d.	10.0	Batch	1.941 ± 0.006	97.08 ± 0.32
		Column	1.996 ± 0.001	99.84 ± 0.06

n.d. = not detectable (LOD of As determination by ICP-OES ≈ 0.05 mg/L)