

## Composite Geological Materials for Treatment of Arsenic in Groundwater

Paveena Kitbutrawat<sup>1</sup>, Waruntorn Kanitpanyacharoen<sup>1\*</sup> and Seelawut Damrongsiri<sup>2</sup>

<sup>1</sup> Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand

<sup>2</sup> Environmental Research Institute, Chulalongkorn University, Bangkok, 10330, Thailand

Corresponding author email: Warunthon.K@chula.ac.th

### Abstract

Arsenic contamination in groundwater is an important problem in many countries and responsible for many life-threatening diseases such as black fever, cancer, neurological and cardiovascular diseases. Despite the proposal of several remediation techniques, it has been challenging to find a cost-effective method to remove arsenic from groundwater in Thailand. This research is thus aimed to study chemical and physical properties of geological materials to create cost-effective adsorbents for arsenic removal. The most effective adsorbent in this study is made of porous siltstone, expanded perlite, and soil sample at the ratio of 66.67 to 16.67 to 16.67, respectively. The adsorbents are first tested with laboratory-based arsenic contaminated water at different conditions to identify the amount of adsorbent and adsorbate that can effectively remove arsenic and understand the underlying mechanisms of adsorption. Results show that the use of 10 grams of adsorbents per 50 ml of adsorbate at the pH of 7 with 2 hours of contact time can remove arsenic up to 41.39%. The value of  $1/n$  from Freundlich adsorption isotherm is 1.27, indicating that the surface of adsorbent is heterogeneous. The energy of sorption from Dubinin – Radushkevich adsorption isotherm is 3.79 kJ/mol, suggesting the kinetic is physical adsorption. In addition, the maximum capacity of adsorbent from Langmuir adsorption isotherm is 0.45 mg/g. Adsorbents are further tested with natural groundwater from 11 wells in Amphoe Dan Chang, Suphan Buri and Amphoe Ban Rai, Uthai Thani, which contain arsenic ranges from 16.13 to 362.3  $\mu\text{g/l}$  and have pH ranges from 6.95 to 7.35. Arsenic can be effectively removed between 20.17% and 75.31%. The variable amount of arsenic removal is likely due to the presence of phosphate, which has a similar structure to arsenite. In addition, the disintegration of adsorbents may release a noticeable amount of magnesium, which in turn inhibits the adsorption of arsenic and decreases the arsenic removal percentage.

**Keywords:** Arsenic, Siltstone, Expanded perlite, Soil sample

### 1. Introduction

Arsenic contaminated groundwater is a leading environmental problem in many countries, particularly in the United States of America, Bangladesh, Nepal, Vietnam, Taiwan, China, South Korea, Japan, and Thailand ((Mukherjee et al., 2006)). High intake of arsenic leads to life-threatening diseases such as black fever, cancer, neurological and cardiovascular diseases, and diabetes (Smedley & Kinniburgh, 2005). Naturally occurring arsenic often arises in rock formations with high volumes of arsenopyrite

(FeAsS) and other sulfide minerals. Arsenic is considered a metalloid and found in many oxidation states, of which arsenic (III) and arsenic (V) being the most common. In Thailand, arsenic contaminated groundwater has been reported in some parts of Amphoe Ron Phibun in Nakorn Si Thammarat (Bavornsachoti, 1995), and arsenic contaminated surface water has been reported in Amphoe Dan Chang in Suphan Buri (Bureau of Mineral Resources Identification and Research, 2013)) and Amphoe Banrai in Uthai Thani

((Bureau of Mineral Resources Identification and Research, 2014).

Arsenic is a metalloid with the atomic number of 33. It occurs in various arsenic-bearing mineral such as orpiment ( $\text{As}_2\text{S}_3$ ), realgar ( $\text{As}_4\text{S}_4$ ), arsenopyrite ( $\text{FeAsS}$ ) and scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) associated with metal ore deposits. In addition, inorganic arsenic compounds can be separated into two groups. The first group forming as arsenite ( $\text{As(III)}$ ), or trivalent compounds such as  $\text{As}_2\text{O}_3$ ,  $\text{NaAsO}_2$ ,  $\text{AsH}_3$ ,  $\text{AsCl}_3$ , and  $\text{As}_2\text{O}_3$ , occurring in a reduction phase. The As-rich rocks are normally weathered in basic environments. As (III) is mobilable in water and may precipitate as a contaminant within layers of alluvial sediments. At pH 0 to pH 9, arsenite is formed as  $\text{H}_3\text{AsO}_3$ , which is a non-polar compound. At pH > 9, arsenite can be formed as  $\text{H}_2\text{AsO}_3^-$  and  $\text{HASO}_3^{2-}$ , which have negative polarity. The second group forming as arsenate ( $\text{As (V)}$ ), or pentavalent compounds such as  $\text{As}_2\text{O}_5$  and  $\text{H}_3\text{AsO}_4$ , are existing in an oxidation phase. In an acid environment, As (V) generally exists and spreads to a large area. In a basic environment, As (V) is normally precipitated with iron oxide and aluminium oxide. At pH 0 to pH 2, arsenate is formed as  $\text{H}_3\text{AsO}_4$ , which is a non-polar form. At pH > 2, arsenate is formed as  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$ , and  $\text{AsO}_4^{2-}$ , which have negative polarity ((Jiang et al., 2013)).

The remediation techniques for arsenic contaminants have been proposed to decrease the impact. One of the remediation techniques is to use geomaterials as adsorbents in arsenic contaminated groundwater. Adsorbents that are made of geological materials can be relatively cheaper than the others methods. Inglethorpe et al. (1999) investigated arsenic adsorbents made from diatomite from Lampang. Diatomites mainly contain opal, which is inert, rigid substrate for arsenic adsorption. Diatomite with iron-stained is used to treat As (V) contaminated water. The kinetic of adsorption is physical adsorption. The behavior should be a monolayer adsorption for As (V). Langmuir

Adsorption Isotherm is used to determine the adsorption capacity for As (V) is 0.23 mg/g.

In this study, siltstone is used in adsorbents because it has porous structure. Heated expanded perlite is another geomaterial that is commonly incorporated in the adsorbents. It can expand 5-20 times. Expanded perlite is also light weight, high porous, and high heat resistant. Soil sample is used to combined siltstone and expanded perlite. Soil sample is the other material to used to adsorbents.

### 1.1 Objective

To investigate physical and chemical properties of geomaterial combination used to make adsorbent for arsenic contaminant removal from groundwater.

## 2. Material and Methodology

### 2.1 Material

The adsorbents used in this study are composed of three main components: siltstone, soil sample, and expanded perlite. Siltstone was collected from a roadcut outcrop near Surasakmontri Hospital in Amphoe Mueang Lampang. Siltstone from this area is generally pale brown to brown and opaque and initially thought to be diatomite. Soil sample was collected from Lampang Kaolin Mining Company Limited in Amphoe Chae Hom, Lampang. Soil sample is very fine-grained and its fresh color is white. Expanded perlite was obtained from Klong Yang Mining in Amphoe Sa-Bot, Lopburi. Perlite is green and its weathering color is pale gray. After heating, perlite turns into white with volume expansion of 5 – 20 times. Siltstone, soil sample, and expanded perlite are grounded down to 100 mesh (0.149 mm.).

### 2.2 Method

All the geological materials are cleaned with deionized water for several times and dry at room temperature. After that, each

geological material is analyzed employing X-ray diffraction (XRD) and X-ray fluorescence (XRF), respectively to identify its mineral and element compositions. Siltstone, soil sample, and expanded perlite powders are mixed with Mixture Design 3 compositions, which is the statistics computer program to determine proportions of adsorbent mixture. Adsorbents are heated at 700°C for 3 hours. Finally, all types of the adsorbents are tested for stability in deionized water. The specific surface area, the pore size distribution and porous volume of a sample are calculated by using Brunauer, Emmett and Teller (BET) Theory. The Cation Exchange Capacity (CEC) of the adsorbent is studied to understand the interaction between negative ion on the adsorbent surface and positive ion.

The varying conditions in this experiment include the contact time, pH of the As contaminated water, and the initial concentration. In the first scenario, the contact times are varied from 15, 30, 45, 60, 90, 120, 150, and 180 minutes for testing with 50 mL of water, 50 ppb of initial As concentration, uses 10 g of adsorbent. In the second scenario uses different pH values from 1, 4, 7, and 10 with 100 ppb of initial As concentration, 10 g of adsorbents, and 120 minutes of contact time. In the third scenario the initial As concentrations are varied from 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 ppb in tests which keep water volume (50 mL), amount of adsorbent (10 g), and contact time (120 minutes). Batch experiment is used to mix between adsorbents and As contaminated water. Solution was shaken at 180 round per minute (rpm) at room temperature. After that, the solution was filtered with filter paper for separate adsorbents and the solution. The solution was measured for As removal using Graphite-Furnace Atomic Absorption Spectroscopy (GFAAS) and calculated the As removal percentage and calculated the As removal percentage by Equation 1.

$$\% \text{ Removal} = \frac{(C_0 - C_e) \times 100}{C_0} \quad \text{Equation 1}$$

Where:

$C_0$  = Concentration in the initial solution

$C_e$  = Concentration after equilibrium

**Table 1** Type of composition of adsorbent.

Type	Expanded perlite	Siltstone	Soil sample
1	100	0	0
2	66.67	33.33	0
3	66.67	0	33.33
4	33.33	66.67	0
5	33.33	33.33	33.33
6	33.33	0	66.67
7	0	100	0
8	0	66.67	33.33
9	0	33.33	66.67
10	0	0	100
11	66.67	16.67	16.67
12	16.67	66.67	16.67
13	16.67	16.67	66.67

### 3. Results

#### 3.1 Molded the adsorbent and dissolution in the water

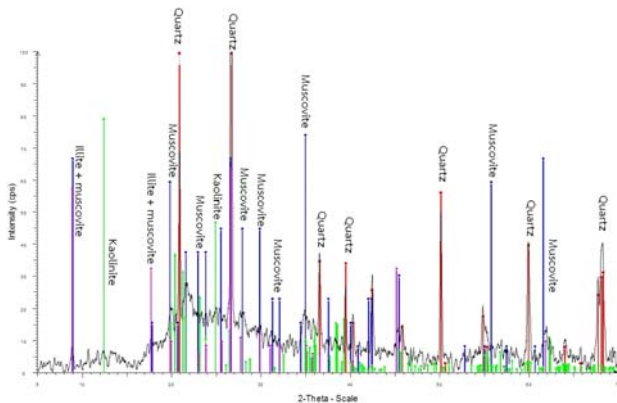
Adsorbent type 12 is composed of expanded perlite (16.67 wt%), siltstone (66.67 wt%), and soil sample (16.67 wt%) and has brown color. Type 12 adsorbent remains intact after drying. After heating adsorbents at 700°C for 3 hours, and submerging them in deionized water, type 12 is the only adsorbent that remains intact after days and the most suitable candidate to test for As removal (Figure 1).



**Figure 1.** The adsorbent type 12

### 3.2 X-ray Diffraction (XRD)

Results from XRD show that the adsorbent type 12 is mainly composed of quartz (red), muscovite (blue), illite (purple) and kaolinite (green) as shown in (Figure 2).



**Figure 2.** A X-ray diffraction pattern of adsorbent type 12.

### 3.3 Chemical Composition

XRF results confirm that the adsorbent type 12 has SiO<sub>2</sub> (69.12%), Al<sub>2</sub>O<sub>3</sub> (15.01%), Fe<sub>2</sub>O<sub>3</sub> (2.57%), and K<sub>2</sub>O (3.52%) as major components. While others oxides are found less than 5% (Table 2).

**Table 2** The chemical composition of raw material (weight percent).

Chemical composition	Adsorbent type 12 (wt %)
SiO <sub>2</sub>	69.12
Al <sub>2</sub> O <sub>3</sub>	15.01
Fe <sub>2</sub> O <sub>3</sub>	2.57
K <sub>2</sub> O	3.52
Na <sub>2</sub> O	0.75
MgO	0.52
TiO <sub>2</sub>	0.42
CaO	0.49
SO <sub>3</sub>	0.62
LOI	6.60
Total	99.61

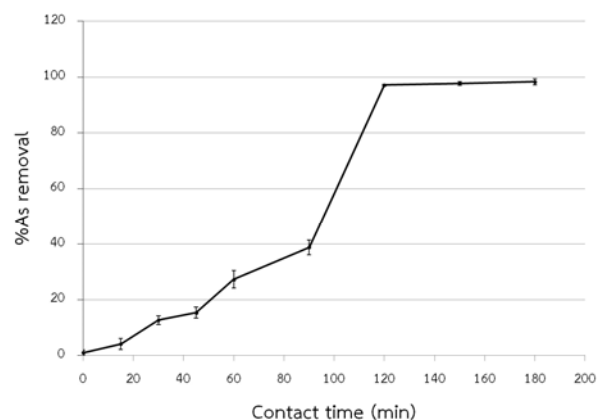
### 3.4 BET Method

Results from BET measurements show that the specific surface area of unheated adsorbent type 12 is 28.2 m<sup>2</sup>/g, the pore volume is 0.097 cm<sup>3</sup>/g., and the average pore size is 137.2 Å (mesopore range). The specific surface area of heated adsorbent type 12 is 32.6 m<sup>2</sup>/g, the pore volume is 0.099 cm<sup>3</sup>/g., and the average pore size is 121.4 Å (mesopore range). The specific surface area and pore volume of heated adsorbent type 12 were increased. However, pore size of heated adsorbent type 12 was decreased.

### 3.5 The efficiency of As removal by GFAAS

#### 3.5.1 Scenario 1 : Effect of contact time

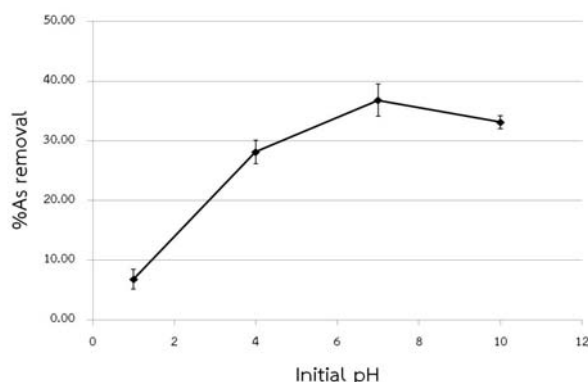
The As(III) removal percentage increases as a function of the contact time, from 4.94 to 10.88, 13.1, 25.7, 39.64 and 97.40%. The arsenic removal efficiency was zero to 4.95% at the contacttime was 0 to 15 minutes. After contacting water more than 2 hours, the adsorption ability becomes saturated as shown by a steady removal percentage of As, which is 97.40% (Figure 3).



**Figure 3.** Arsenic removal percentage as a function of the contact time.

### 3.5.2 Scenario 2 : Effect of pH

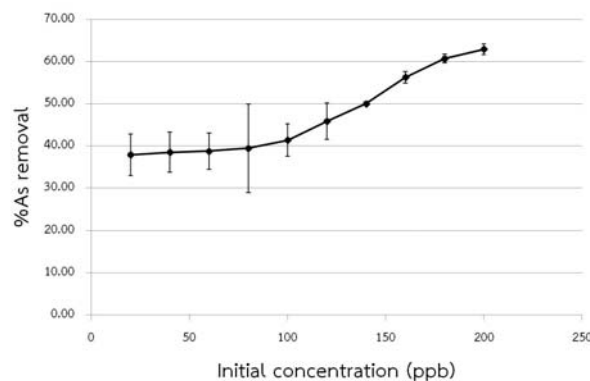
The arsenic removal percentage increases as a function of the pH, when the pH value is higher, from 6.81 to 28.16, 36.81% for the initial concentration of 100 ppb. However, when the pH value is 10 the arsenic removal percentage decreases to 33.13%. From the study of variable pH, arsenic can be best removed when the pH of solution is around 7 (Figure 4).



**Figure 4.** Arsenic removal by varying pH value.

### 3.5.3 Scenario 3 : Effect of concentration of As

The arsenic removal percentage increases as a function of the initial concentration, from 37.92 to 38.50, 38.79, 39.45, and 41.39%. The As removal percentage trends to be constant, after the concentration is 100 ppb, the As removal percentage rises in slowly, and decreases. This result is conflicted with the previous test, because of the initial pH of the As contaminated waters are different. The initial pH of the first As contaminated water is 1.52, but the initial pH of the second As contaminated water is adjusted to 7. (Figure 5).



**Figure 5.** Arsenic removal percentage as a function of the concentration.

### 3.6 The cation exchange capacity (CEC)

The cation exchange capacity (CEC) is the value of the ability that is the reaction between the ion of the adsorbent surface and the solution. The CEC of adsorbent type 12 is 10.94 cmol/kg. The CEC of raw material, that are siltstone (2.07 cmol/kg), soil sample (4.91 cmol/kg.), and expanded perlite (20.14 cmol/kg.).

### 3.7 The adsorption isotherm

The adsorption test performed to find suitable conditions for As treatment such as variation of pH, initial concentration, and contact time. Suitable conditions refer to the conditions at which adsorption, for this study is used 10 grams of adsorbents for the solution 50 ml in pH 7. The contact time is 2 hours. The adsorption mechanism is studied by varying initial concentration and plotted the graph of solid-liquid distribution coefficient. The amount of As adsorbed ( $q_e$ ) was calculated by Equation 2.

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad \text{Equation 2}$$

Where:

$C_0$  = Concentration of As in the initial solution ( $\mu\text{g/L}$ )

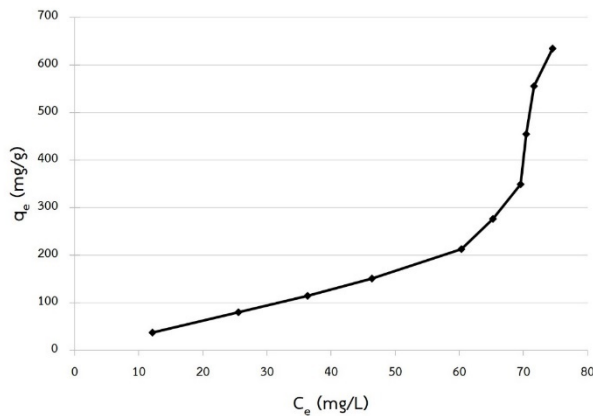
$C_e$  = Concentration of As after equilibrium ( $\mu\text{g/L}$ )

$q_e$  = Amount of metal adsorbed (mg/g)

$K$  = Solid – liquid distribution coefficient

$V$  = Volume (l)

$m$  = mass (kg.)



**Figure 6.** A graph of solid – liquid distribution coefficient.

The slope of the graph of solid-liquid distribution coefficient gradually increases at low As concentrations (10-60 mg/L) and exponentially rises at high As concentrations (60-80 mg/L) (Figure 6). According to Weber and Chakravorti (1974), the shape of graph curve implies to unfavorable that means the interaction between adsorbents and adsorbate was reversible because of the adsorbate was desorbed from the adsorbents.

### 3.7.1 The Langmuir Adsorption Isotherm

Langmuir adsorption isotherm is used to describes the mechanism adsorption, which the surface of adsorbent is a perfectly flat plain and homogeneous. The adsorbent can adsorped one element on to monolayer, and do not have interaction between adsorbate molecules. The mechanism of adsorption ( $R_L$ ) is calculated by Equation 3.

$R_L$  value is indicated the mechanism of adsorption. If  $R_L$  is more than 1, the mechanism of adsorption is unfavorable. If  $R_L$  is 1, the mechanism of adsorption is linear. If  $R_L$  is range from 0 to 1, the mechanism of adsorption is favorable. Moreover, if  $R_L$  is 0, the mechanism adsorption is irreversible.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 K_L C_e} \quad \text{Equation 3}$$

Where :

$C_0$  = Concentration in the initial solution (mg/L)

$C_e$  = the Concentration after equilibrium (mg/L)

$q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

$Q_0$  = maximum monolayer coverage capacity (mg/g)

$K_L$  = Langmuir isotherm constant (L/mg)

$1/Q_0 K_L$  = Slope of a graph

$V$  = Volumn (l)

$m$  = mass (kg.)

**Table 3.** The constant that calculated form Langmuir Adsorption Isotherm.

Constant	Value
$1/Q_0$	0.22
$Q_0$ (mg/g)	0.45
$K_L$ (L/mg)	6.11
$R_L$	1.12 – 2.21
$R^2$	0.98

### 3.7.2 The Freundlich Adsorption Isotherm

Freundlich adsorption isotherm is used to describe the mechanism of adsorption, where the surface of the adsorbent is heterogeneous. The adsorbent can adsorb more than one layer, and the adsorbate molecules are interact to the adsorbents. Freundlich adsorption isotherm is also written as Equation 4, and the function of the strength of adsorption process ( $1/n$ ) and Freundlich isotherm

constant are calculated from the graph of Freundlich adsorption isotherm. A function of the strength of adsorption process can be calculated from  $1/n$  value. If  $n$  is equal to 1, the partition between the two phases are independent of the concentration. If  $1/n$  value is below 1, it means a normal adsorption. If  $1/n$  value is more than 1, it means cooperative adsorption. The cooperative adsorption refers to the interaction between adsorbent and adsorbate or between adsorbates ((Liu, 2015)).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \text{Equation 4}$$

Where:

$q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

$K_f$  = Freundlich isotherm constant (mg/g)

$C_e$  = the equilibrium concentration of adsorbate (mg/L)

$1/n$  = Slope of a graph

**Table 4.** The constant that calculated form Freundlich Adsorption Isotherm.

Constant	Value
$1/n$	1.27
$n$	0.79
$K_f$ (mg/g)	1.47
$R^2$	0.90

#### 4.2.3 The Dubinin – Radushkevich Adsorption Isotherm

Dubinin-Radushkevich equation is modified from Freundlich adsorption isotherm and used to describe the adsorption mechanism with a micropore volume filling on the heterogeneous adsorbent surface. Dubinin-Radushkevich equation is also written as Equation 5

$$\ln q_e = \ln q_s - K_{ad}\epsilon^2 \quad \text{Equation 5}$$

$$E = \frac{1}{\sqrt{2BD}} \quad \text{Equation 6}$$

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad \text{Equation 7}$$

Where:

$q_e$  = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

$q_s$  = theoretical isotherm saturation capacity (mg/g)

$K_{ad}$  = Dubinin – Radushkevich isotherm constant (mol<sup>2</sup>/kJ<sup>2</sup>)

$E$  = Energy of sorption (kJmol<sup>-1</sup>)

$B_D$  = Isotherm constant

$\epsilon$  = Dubinin – Radushkevich isotherm constant

$R$  = Universal gas constant that is 8.314 J/mol/K

$T$  = Temperature at 298 K

**Table 6.** The constant that calculated form Dubinin-Radushkevich Adsorption Isotherm.

Constant	Value
$\ln q_s$	5.74
$q_s$ (mg/g)	0.31
$B_D$	0.0347
$E$ (kJ/mol)	3.79
$R^2$	0.8644

The adsorption mechanism on the adsorbent have two types. First is the physical adsorption that is the interaction between the arsenic and the adsorbent surface. The second is a chemical adsorption that is when the adsorbate is reacts to adsorbent and changes the structure or chemical composition of adsorbent. From the Dubinin-Radushkevich isotherm, the energy of adsorption is 3.79 kJ/mol, which indicates that the mechanism of adsorption is physical adsorption. The physical adsorption is not necessary to use high energy. The maximum capacity of adsorbent from Langmuir adsorption isotherm is 0.45 mg/g. The value of  $1/n$  from Freundlich adsorption

isotherm is 1.27, indicating that the surface of adsorbent is heterogeneous.

### 3.8 Analyze qualitative of As contaminated groundwater

**Table 7.** The result of removal percentage of arsenic contaminated groundwater.

Sample	C <sub>0</sub>	C <sub>e</sub>	% As Removal
GW01	139.33	99.67	28.46
GW02	17.10	8.60	49.71
GW03	26.24	9.39	64.21
GW04	147.00	36.30	75.31
GW05	42.67	32.00	25.01
GW06	80.33	50.33	37.35
GW07	38.70	15.20	60.72
GW08	362.30	259.00	28.51
GW09	39.67	31.67	20.17
GW10	93.80	38.20	59.28
GW11	16.13	8.08	49.91

### 4. Discussion

**Table 8.** The comparison of maximum capacity, specific surface area, and cation exchange capacity of adsorbent.

Material	C <sub>0</sub> (mg/g)	Surface area (m <sup>2</sup> /g)	CEC (cmol/kg)
Bentonite	28.2 <sup>1</sup>	40 – 130 <sup>2</sup>	0.83 – 0.94 <sup>3</sup>
Zeolite	0.97 <sup>4</sup>	600 – 900 <sup>5</sup>	80 – 120 <sup>6</sup>
Studied adsorbent	0.45	32.6	10.94

<sup>1</sup> Zahra et al., 2009, <sup>2</sup> Kaufhold et al., 2010, <sup>3</sup> Kiviranta and Kumpulainen, 2011, <sup>4</sup> Branislava et al., 2011, <sup>5</sup> Isao et al, 1986, and <sup>6</sup> ZEO INC., 2014

From the Table 8, the adsorbent Type 12 has the lowest value of the maximum capacity for As. The specific surface area of

our adsorbent is small (32.6 m<sup>2</sup>/g). Other geological materials such as zeolite has high specific surface area (600 - 900 m<sup>2</sup>/g) and CEC (80 – 120 cmol/kg). Bentonite is another geomaterial adsorbent, which has maximum capacity for As (28.2 mg/g) but low specific surface area (40 - 130 m<sup>2</sup>/g) and CEC (0.83 – 0.94 cmol/kg) values.

From the Table 7, the arsenic contaminated groundwater is different in each well. A previous study by Bureau of Mineral Resources Identification and Research (2013) and Bureau of Mineral Resources Identification and Research (2014) of heavy metal contaminated in Suphan Buri and Uthai Thani, the arsenic contamination in surface water, soil and the alluvial sediment are found at the boundary of Amphoe Dan Chang in Suphan Buri and Amphoe Ban Rai in Uthai Thani. The geology of this area is contact metamorphism between granite and limestone, sedimentary rocks and metamorphic rocks such as marble and quartz-mica schist Bureau of Mineral Resources Identification and Research, 2014. This area is the potential resource of tin. The tin mine is the important source of arsenic contamination, because the associated mineral of cassiterite such as arsenopyrite (FeAsS) is the important source of arsenic. The other source of arsenic is arsenic compounded agriculture fertilizer.

The arsenic contamination in groundwater was found in the shallow aquifers, because they contaminated with soil by arsenic compounded agriculture fertilizer. The effect of pH is the first condition to study the As contamination and the As removal. The As(V) removal was decreased with increasing pH. In addition, pH 3 is the most effectively of As(V) removal. As(III) has a maximum adsorption in the solution with pH equal to 7 (Yoon et al., 2015). In this study, the pH values are not significant variations because the pH values of every groundwater wells were similar and assumed is the same value as the suitable condition (pH equal to 7).

The interesting variant is the type of arsenic. The arsenic contaminated in



groundwater can separate in 2 types, that are As(III) and As(V).  $H_3AsO_3^0$  is the dominant As(III) species at pH is lower than 8, which is neutral type. At the pH is more than 8,  $H_2AsO_3^-$  is the dominant As(III) species.  $H_2AsO_4^-$  is the dominant inorganic As(V) species at pH is lower than 7, and at the pH is more than 7,  $HAsO_3^{2-}$  is the dominant As(V) species (Bangladesh Consortium For Arsenic Management, 2017). Boyle and Jonasson (1973) suggest that As(V) is contaminated in an oxidation phase water.

The As(V) are better adsorped than As(III) because at pH equal 6 – 8, As(V) that is negatively charged ( $H_2AsO_4^-$  and  $HAsO_3^{2-}$ ) has a stronger electrostatic than As(III) that is neutral ( $H_3AsO_3^0$ ). Therefore As(V) are remediated better than As(III) (Jiang et al., 2013). The total dissolved solid (TDS) values may affect the adsorption capacity, because cations and anions can react and form complex structures with the adsorbent surface. The anion that can affect arsenic removal is phosphate ( $PO_4^{3-}$ ) due to its similar molecular structure as arsenate. Violante and Pigna (2002), reported that Al-rich mineral such as clay mineral, have a greater adsorption for phosphate than arsenate. Jain and Loeppert (2000) suggested that phosphate can effect to arsenate adsorption at the high pH as shown in and Table 9 (Manning and Goldberg, 1997)

**Table 9.** The result of removal percentage of phosphate

Sample	pH	C <sub>0</sub> (ppm)	C <sub>e</sub> (ppm)	% PO <sub>4</sub> <sup>3-</sup> removal
GW01	7.15	22.56	18.61	17.51
GW02	6.95	12.87	10.54	18.10
GW03	7.05	12.86	10.32	19.75
GW04	7.25	26.98	23.96	11.19
GW05	7.18	15.51	10.74	30.75
GW06	7.03	11.82	7.52	36.38
GW07	7.16	26.87	15.26	43.21
GW08	7.01	42.53	39.34	7.50

GW09	7.25	21.91	18.94	13.56
GW10	7.35	23.89	21.76	8.92
GW11	7.08	17.43	15.55	10.79

The volumes of potassium, calcium, magnesium, and sodium increase after groundwater treatment with our adsorbent likely due to the the disintegration of adsorbents. The significant increases of potassium volumes largely affect the arsenic removal capacity. The arsenic removal percentages generally decrease after adding adsorbents (Table 10).

**Table 10.** The result of potassium increasing percentage.

Sample	C <sub>0</sub> (ppm)	C <sub>e</sub> (ppm)	% K increase
GW01	3.94	41.48	951.55
GW02	6.13	14.87	142.58
GW03	2.69	10.75	299.63
GW04	9.19	21.76	136.78
GW05	2.65	39.10	1376.83
GW06	5.42	43.07	694.89
GW07	7.97	44.21	454.71
GW08	0.72	39.73	5440.68
GW09	0.59	41.20	6874.60
GW10	7.22	31.96	342.66
GW11	6.13	18.65	204.24

## 5. Conclusion

1. Based on XRD and XRF analyses, the geomaterial adsorbent is mainly composed of quartz, kaolinite, and iron oxide mineral such as goethite. The specific surface area is quite low at 32.6 m<sup>2</sup>/g. The adsorbent surface is heterogeneous due to high 1/n value (1.27) of Freundlich Adsorption Isotherm. In addition, SEM images show different grain sizes and shapes of adsorbents.

2. The most optimized conditions for removing As(III) is to use 10 grams of geomaterial adsorbents with a 50 ml solution in pH 7 for 2 hours. The energy of sorption is physisorption (van der Waals) interpreted by the shape of the solid – liquid distribution coefficient graph that has the “unfavorable shape”. Energy of sorption value from Dubinin – Radushkevich Adsorption Isotherm ( $E < 8$ ), it is a physisorption. The CEC value is 10.94 cmol/kg, it is very low, that shows the adsorption is physisorption. The maximum capacity of this study geomaterials for As(III) removal is 0.45 mg/g.

3. Under the optimized conditions, the geomaterial adsorbents can remove arsenic between 20.71 and 75.31% from contaminated groundwater wells.

4. The cost of the adsorbent is very cheap as the price of the raw materials is low. The approximate price is 20 THB per 100 kg of adsorbents. This geomaterial adsorbent thus presents an alternative, environmental-friendly, and cost-effective method for arsenic contaminated water treatment in Thailand.

## 6. Recommendation for future studies and researches.

Other geological materials such as zeolite, and pumice that has high porous structure and are abundant in Thailand should be evaluated. In addition, the particle size of geomaterials should be varied and tested to improve the efficiency of adsorbents. These adsorbents should be further tested with other heavy metal in contaminated groundwater to maximize the advantage of adsorbents.

The effects of cation and anion for As (III) adsorption should be studied. Because in this study, the As (III) concentration is quite small, the impact of the other cation and anion are not significant. The inorganic As contaminated groundwater is mainly composed of As (III) and As(V). The instrument that can separate the type of As is High-Performance

Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP-MS).

## REFERENCES

- Ahmed, F. M. (2001). An overview of arsenic removal technologies in Bangladesh and India. 19.
- Akutsu, J. (1979). On the Fossil diatoms from Amphoe Muang, Changwat Lampang, Thailand. *Contributions to the Geology and Paleontology of Southeast Asia*, 3.
- Al-Degs, Y. S., Tutunju, M. F., & Shawabkeh, R. A. (2000). The Feasibility of Using Diatomite and Mn-Diatomite for Remediation of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  from Water. *Separation science and Technology*, 35(14), 12.
- Alkan, M., & Dogan, M. (2001). Adsorption of Copper (II) onto Perlite. *Journal of Colloid and Interface Science*, 243(2), 12.
- Athikom-rangsarit, S. (1994). Arsenic contamination in Ground Water From Seven Province of Thailand. 38.
- Bangladesh Consortium For Arsenic Management. (2017). Aqueous Inorganic Arsenic. Retrieved from <http://arsenic.tamu.edu/about/course/mod2/notes/pg3.htm>
- Barakat, M. A. (2011). New Trends in Removing Heavy Metals from Industrial Wastewater. *Arabian Journal of Chemistry*, 4(4), 17.
- Bavornsachoti, P. (1995). Arsenic contamination in Water. *Department of Mineral Resources, Thailand*, 33(2), 5.
- Boss, C. B., & Fredeen, K. J. (2004). Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry. 120.
- Boyle, R. W., & Jonasson, I. R. (1973). Geochemistry of arsenic and its use as indicator element in geochemical prospecting. *Journal of Geochemical Exploration*, 2(3), 46.
- Branislava, M. J., Vesna, L. V., Dorde, N. V., & Ljubinka, V. R. (2011). Arsenic Removal from water using low-cost

- adsorbents- a comparative study. *Journal of the Serbian Chemical Society*, 76(10), 16.
- Broome, S. W. (2012). Cation Exchange (Lecture). from North Carolina State University  
<http://broome.soil.ncsu.edu/ssc012/Lecture/topic14.htm>
- Bureau of Mineral Resources Identification and Research. (2013). The Risk area from Natural Contamination, Changwat Suphanburi. *1*(1), 174.
- Bureau of Mineral Resources Identification and Research. (2014). The Risk area from Natural Contamination, Changwat Uthai Thani. *1*(1), 150.
- Chaisam, U., & Nissapha, Y. (1994). Standard of Minerals for Application and Trade. 320.
- Chakir, A., Bessiere, J., Kacemia, K., & Marouf, B. (2002). A Comparative Study of The Removal of Trivalent Chromium from Aqueous Solutions by Bentonite and Expanded Perlite. *Journal of Hazard Material*, 95, 18.
- Cheungyuesuk, N., & Suriyachai, P. (1987). Geological Survey Report : Ban Mahaphoe (5139I), Amphoe Sri Thep (5239IV), Ban Pa-niad (5139II), and Amphoe Chai-badan (5239III). 85.
- Department Mineral Resources Thailand. (2017). Kaolinite. Retrieved from <http://www.dmr.go.th/main.php?filena me=kaolinite>
- Department of Mineral Resources Thailand. (2007). Geological Map of Changwat Lampang. 1.
- Department of Physics Warwick University. (2010). Scanning Electron Microscopy (SEM).  
<http://text.www2.warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpag s/ex5/techniques/structural/sem3>
- Department of Primary Industries and Mines Thailand. (2017). Daily Mineral Price. from Department of Primary Industries and Mines, Thailand  
<http://www.dpim.go.th/minerals-minerals/mp004.php>
- Department of Statistics Online Programs. (2017). Mixture Designs in Minitab. <https://onlinecourses.science.psu.edu/stat503/node/61>
- Dogan, M., Alkan, M., & Onganer, Y. (2000). Adsorption of Methylene Blue from Aqueous Solution onto Perlite. *Water, Air, and Soil Pollution*, 120(3), 20.
- Donahue, R. L., Miller, R. W., & Shickluna, J. C. (1977). Soils: An Introduction to Soils And Plant Growth. 667.
- Elizalde-Gonzalez, M. P., Mattusch, J., Wennrich, R., & Morgenstern, P. (2001). Sorption on Natural Solids from Arsenic Removal. *Journal of Chemical Engineering*, 81(9), 187.
- Gunning, D. F. (1994). Perlite Market Study. *Ministry of Energy, Mines and Petroleum Resources, Mineral Resources Division, Geological Survey Branch*(Open-File Report 1994-21), 97.
- Herskovitch, D., & Lin, I. J. (1996). Upgrading of Raw Perlite by A Dry Magnetic Technique. *Magnetic and Electrical Separation*, 7, 17.
- Hinkle, S. R., & Polette, D. J. (1999). Arsenic in Ground Water of the Willamette Basin, Oregon. 34.
- Hung, P. A., & Hai, N. X. (2013). Synthetic of Zeolite from Natural Diatomite Bao Loc District, Lam Dong Province of Vietnam and Application for Heavy Metal Removal (Pb and Cd). *Journal of Agricultural and Biological Science*, 8(8), 6.
- Inglethorpe, S. D. J., & Morgan, D. J. (1992). The Laboratory Assessment of Diatomite. *Geologic Resources of Thailand: Potential for Future Development*, 210-221.
- Inglethorpe, S. D. J., & Pearce, J. M. (1999). Mineralogy and Petrography of Diatomite from the Lampang Basin, Changwat Lampang, Northern Thailand. *99*(33), 29.
- Inglethorpe, S. D. J., Utha-aroon, C., & Chanyavanich, C. (1998). An Inventory of The Diatomite Deposits of The

- Lampang Basin, Changwat Lampang, Northern Thailand. 98(33), 28.
- Inglethorpe, S. D. J., Whitbread-Abrutat, P. H., & Metcalfe, R. (1999). An Investigation of the Sorption of Arsenic by Diatomite. 99(20), 32.
- Isao, S., & Shoichi, O. (1986). Determination of external surface areas of zeolites. *Journal of Catalysis*, 100(1), 9.
- Jalil, M. A., & Ahmed, M. F. (2001). Development of An Activated Alumina Based Household Arsenic Removal Unit. *Technologies for Arsenic Removal From Drinking Water*, 15.
- Jiang, J. Q., Ashekuzzaman, S. M., Jiang, A., Sharifuzzaman, S. M., & Chowdhury, S. R. (2013). Arsenic Contaminated Groundwater and Its Treatment Options in Bangladesh. *Journal of Environmental Research and Public Health*, 10(1), 29.
- Jungyusuk, N., & Khositantont, S. (1992). Volcanic Rocks and Associated Mineralization in Thailand. *Geologic Resources of Thailand: Potential for Future Development*, 17.
- Kabra, S., Katara, S., & Rani, A. (2013). Characterization and study of turkish perlite. *International journal of innovative research in science engineering and technology*, 2(9), 8.
- Katsoyiannis, I., Zouboulis, A., Althoff, H., & Bartel, H. (2002). As(III) Removal from Groundwater Using Fixed-bed Upflow Bioreactors. *Chemosphere*, 47, 8.
- Kaufholda, S., Dohrmanna, R., Klinkenbergc, M., Siegesmundd, S., & Ufere, K. (2010). N<sub>2</sub>-BET specific surface area of bentonites. *Journal of Colloid and Interface Science*, 349(1), 8.
- Kiviranta, L., & Kumpulainen, S. (2011). Quality Control and Characterization of Bentonite Materials. (Working Report 2011-84), 102.
- Kumanchan, P. (1979). Bentonite. *Geology Society Thailand*(Special Issue), 6.
- Kumanchan, P., & Traiyan, A. (1986). Research on geologic environment, chemical compositions, physical properties and the uses of diatomite from the Lampang Basin, northern Thailand. 27.
- Lee, S. H., Kim, K. W., Lee, B. T., Bang, S., Kim, H., Kang, H., & Jang, A. (2015). Enhanced Arsenate Removal Performance in Aqueous Solution by Yttrium-Based Adsorbents. *Journal of Research and Public Health*, 12, 18.
- Liu, S. (2015). Cooperative adsorption on solid surfaces. *Journal of Colloid and Interface Science*, 450, 15.
- Maji, S. K., Pal, A., Pal, T., & Adak, A. (2007). Sorption Kinetics of Arsenic on Laterite Soil in Aqueous Medium. *Journal of Environmental Science and Health. Part A*, 42(7), 8.
- Manning, B. A., & Goldberg, S. (1997). Adsorption and Stability of Arsenic(III) at The Clay Mineral - Water Interface. *Journal of Environmental Science Technology*, 31(7), 7.
- Mathialagan, T., & Viraraghavan, T. (2002). Adsorption of cadmium from aqueous solutions by perlite. *Journal of Hazardous Materials*, 94(3), 13.
- Matis, K. A., Zouboulis, A., Zamboulis, P., & Valtadorou, A. V. (1999). Sorption of As(V) by Geothite Particles and Study of Their Flocculation *Water, Air, and Soil Pollution*, 111(20), 297.
- Meesuk, L., & Seammai, S. (2010). The Use of Perlite to Remove Dark Colour from Repeatedly Used Palm Oil. *Science Asia*, 36, 7.
- Mines, D. o. P. I. a. (1998). Industrial Minerals and Its Properties. . 271.
- Mostafa, M. G., Chen, Y. H., Jean, J. S., Liu, C. C., & Lee, Y. C. (2011). Kinetics and Mechanism of Arsenate Removal by Nanosized Iron Oxide-coated Perlite. *Journal of Hazardous Materials*, 187(1-3), 7.
- Mukherjee, A., Sengupta, M. K., Hossain, M. A., Ahamed, S., Das, B., Nayak, B., . . . Chakraborti, D. (2006). Arsenic Contamination in Groundwater: A Global Perspective with Emphasis on

- the Asian Scenario. *Journal of Health, Population and Nutrition*, 24(2), 22.
- Nakwanit, S. (2010). Waste Management of Arsenic Accumulated Plants at Ron Phibun District, Nakorn Si Thammarat Province, Thailand. *Graduated Studies, Ph.D. (Biology)*, 171.
- Niesz, K., Yang, P., & Somorjai, G. A. (2005). Sol-gel synthesis of ordered mesoporous alumina. *Chemical Communication*, 2.
- Noble, R. D., & Terry, P. A. (2004). Principles of Chemical Separations with Environmental Applications. 319.
- Owen, R. B., & Utha-aroon, C. (1992). Diatomaceous sedimentation in the Tertiary Lampang Basin, Northern Thailand. *Journal of Paleolimnology*, 22(1), 15.
- Panthi, S. R., & Wareham, D. G. (2011). Removal of Arsenic From Water Using The Adsorbent : New Zealand Iron-sand. *Journal of Environmental Science and Health, Part A*, 46(13), 6.
- Pariwatawon, P. (1962). Diatomite Deposits in Changwat Lampang. 7.
- Pookmanee, P., Thippraphan, P., & Phanichphant, S. (2011). Removal of Heavy Metals from Aqueous Solution by Natural and Modified Diatomite. *Journal of the Microscopy Society of Thailand*, 4(2), 5.
- Premmanee, J., & Wijitchareampong, A. (1997). Mineral Exploration in Lumnarai Area. 191.
- Ramaswami, A., Tawachsupa, S., & Isleyan, M. (2001). Batch-mixed Iron Treatment of High Arsenic Water. *Water Research*, 35(18), 6.
- Ratanasthien, B. (1992). Neogene Events Recorded in Coalfields in Northern Thailand. *Development Geology for Thailand into The Year 2000*, 15.
- Rayment, G. E., & Higginson, F. R. (1992). Soil and Water Chemical Methods. *Australian Soil and Land Survey Handbooks Series*, 330.
- Saisutthichai, D. (2006). Physical and Chemical Properties of Perlite and Its Application. 43.
- Samar, M., & Saxena, S. (2016). Study of Chemical and Physical Properties of Perlite and Its Application in India. *International Journal of Science Technology and Management*, 5(4), 11.
- Sangpairoj, M. (2006). Diatomite Quality Improvement by Calcination for Removal of Arsenic From Contaminated Water. *Environmental Science (Interdisciplinary Program), Master*, 129.
- Sanlayapong, S. (2017). Rock - Mineral: Lamnarai Volcanoes, Perlite, Pumice, and Pumiceous Tuff, Changwat Loburi - Phetchabun and Its Application 48.
- Seammai, S. (2008). XRD for Mineralogy of Perlite. 41.
- Sharmin, N. (2001). Arsenic Removal Processes on Trial in Bangladesh. *Technologies for Arsenic Removal from Drinking Water*, 8.
- Silukkapatti. (2014). I-XRD-DIAGRAM1.GIF. <https://silukkapatti.wordpress.com/2014/04/16/i-xrd-diagram1-gif/>
- Smedley, P., & Kinniburgh, D. G. (2005). Groundwater and The Environment. *Essentials of Medical Geology*, 35.
- Sonon, L. S., Kissel, D. E., & Saha, U. (2014). Cation Exchange Capacity and Base Saturation. *UG.A. Extension Circular*, 4.
- Teas, C., Kalligeros, S., Zanicos, F., Stournas, S., Lois, E., & Anastopoulos, G. (2001). Investigation of The Effectiveness of Absorbent Materials in Oil Spills Clean Up. *Desalination*, 140, 6.
- Tian, L., Zhang, J., Shi, H., Li, N., & Ping, Q. (2016). Adsorption of Malachite Green by Diatomite: Equilibrium Isotherms and Kinetic Studies. *Journal of Dispersion Science and Technology*, 37(7), 8.
- Torab-Mostaedi, M., Ghassabzadeh, H., Ghannadi-Maragheh, M., Ahmad, & Taher, S. J. (2010). Removal of cadmium and nickel from aqueous

- solution using expanded perlite, Brazilian. *Journal of Chemical Engineering*, 27(2), 10.
- Tsai, W. T., Hsien, K. J., Chang, Y. M., & Lo, C. C. (2005). Removal of herbicide paraquat from an aqueous solution by adsorption onto spent and treated diatomaceous earth. *Bioresour Technology*, 96(6), 7.
- Tsai, W. T., Hsien, K. J., & Yang, J. M. (2004). Silica adsorbent prepared from spent diatomaceous earth and its application to removal of dye from aqueous solution. *Journal Colloid Interface Science*, 275(2), 6.
- Tsai, W. T., Lai, C. W., & Hsien, K. J. (2006). Characterization and Adsorption Properties of Diatomaceous Earth Modified by Hydrofluoric Acid Etching. *Journal Colloid Interface Science*, 297(2), 6.
- Verma, A. (2014). Graphite furnace atomic absorption spectroscopy. <https://www.slideshare.net/AnuradhaKVerma/graphite-furnace-atomic-absorption-spectroscopy>
- Vu, K. B., Kaminski, M. D., & Nunez, L. (2003). Review of Arsenic Removal Technologies for Contaminated Groundwater. 43.
- Weber, T. W., & Chakravorti, R. K. (1974). Pore and solid diffusion models for fixed-bed adsorbers. *AIChE Journal*, 20, 11.
- Wolska, J. A., & Vrebos, B. A. R. (2004). XRF: A Powerful Oil Analysis Tool. <http://www.machinerylubrication.com/Articles/Print/602>
- Wu, C. C., Wang, Y. C., Lin, T. F. L., & Chen, P. C. (2005). Removal of Arsenic From Waste Water Using Surface Modified Diatomite. *Journal of Chinese Institute of Environmental Engineering*, 15(4), 7.
- Yong, R. N., Warkentin, B. P., Phadungchewit, Y., & Galvez, R. (1990). Buffer capacity and lead retention in some clay materials. *Water, Air, and Soil Pollution*, 53, 15.
- Yoon, Y., Park, W. K., Hwang, T. M., & Kang, J. W. (2015). Comparative evaluation of magnetite-graphene oxide and magnetite-reduced graphene oxide composite for As(III) and As(V) removal. *Journal of hazardous materials*, 304, 9.
- Zahra, N., Sheikh, S. T., Mahmood, A., & Javed, K. (2009). Removal of Arsenic From Wastewater Using Bentonite. *Journal of Scientific and Industrial Research*, 44(1), 6.
- ZEO INC. (2014). Retrieved from <http://zeoinc.com/ecosand/cec/>