

Modification of Natural Common Clays as Low Cost Adsorbents for Arsenate Adsorption

Borano Te, Boonchai Wichitsathian, and Chatpet Yossapol

Abstract—In this study, natural common clays were used as raw materials to be modified with ferric and ferrous solutions to develop improved efficient and low cost adsorbents. The adsorbents (Raw Clay, Clay/FeSO₄, and Clay/FeCl₃) were investigated for arsenate removal from synthetic aqueous solution in batch studies with respect to contact time, solution pH, initial As(V) concentration, and temperature. The results showed that As(V) uptake was pH dependent and the high efficiency occurred in the acidic condition. The adsorption kinetic data were fitted well with the pseudo second order adsorption model. The estimated maximum adsorption capacity from Langmuir model was 0.44, 1.50, and 0.86 mg/g for Raw Clay, Clay/FeSO₄, and Clay/FeCl₃, respectively. The values of a dimensionless constant separation factor (R_L) and the magnitude of the adsorption intensity ($1/n$) showed that As(V) was adsorbed favorably on all adsorbents. The thermodynamic parameters indicated that the adsorption is spontaneous and endothermic and an irregular increase of the randomness at the adsorbent-adsorbate interface during the adsorption.

Index Terms—Natural common clays, adsorbent, adsorption, arsenate.

I. INTRODUCTION

Arsenic (As) found in the environment media, in particular in drinking water sources, is one of the major problematic issues for human health due to its toxicity and carcinogenicity [1]. Human health problems associated with excessive and long-term exposure to As are acute and chronic health issues and arsenicosis including skin problems, skin cancers, internal cancers (bladder, kidney and lung), leg and feet blood vessel diseases, and possibly diabetes, high blood pressure, reproductive disorders, adverse pregnancy outcomes, and a decrease in children's intellectual function [2], [3]. More than 70 countries are reported with natural As contamination posing a serious health hazard to an estimated 150 million people, around 110 million of which live in Bangladesh, Cambodia, China, India, Laos, Myanmar, Nepal, Pakistan, Taiwan and Vietnam [4]. European Commission (EC), US Environmental Protection Agency (USEPA), and World Health Organization (WHO) have lowered the permissible limit level of AS in public water supplies to 10 ppb from 50 ppb [5], [6].

Arsenic mostly occurs in the form of arsenate, As(V), and arsenite, As(III). Arsenate generally predominates in

oxygen-rich environments like surface water, whereas arsenite is favored and predominates in a moderately reducing environment with anoxic conditions like in anaerobic groundwater [7], [8]. Arsenite can be oxidized to arsenate [9]. Several technologies reported to remove arsenic from water include coagulation-flocculation, ion exchange, membrane technologies, reverse osmosis and adsorption processes [10]. Adsorption is more advantageous over other As removal technologies in terms of simplicity, economy, removal efficiency, easiness in operation and maintenance, flexibility to be scaled up (from the point of use to a municipal water treatment plant), and avoidance of liquid waste generation on site [6], [11], [12]. Low cost materials have gained increasing interest to be used as adsorbents for As removal from water to reduce the operational costs.

Clays have received more attention as the low cost adsorbents in removing water pollutants such as metal ions, organic pollutants and bacteria due to their wide availability, low cost and good adsorption behavior [12]–[14]. Clays are good adsorbents because of their large specific surface area, chemical and mechanical stability, layered structure, and high cation exchange capacity [14], [15]. However, raw clays express low adsorption of some anionic pollutants due to the negative charges on the surface [16]. For instance, clay minerals such as kaolinite, montmorillonite, and illite exhibits arsenate adsorption in the range of 0.15 to 8.4 $\mu\text{mol/g}$, which is much lower than iron containing minerals such as ferrihydrite and goethite possibly adsorbing arsenate in the range of around 200 $\mu\text{mol/g}$ to 700 $\mu\text{mol/g}$ [17]. Thus, raw clays can be modified or bind to other metal ions like irons to improve the adsorption capacity [18], [19]. So far of our knowledge, no study has addressed the use of natural common clays to support iron species to be more cost-effective and efficient adsorbents for arsenate removal from water.

The purpose of this study was to assess the As(V) adsorption of raw clay and iron modified natural common clays from aqueous solution with respect to contact time, solution pH, initial As(V) concentration, and temperature, and to evaluate the As(V) adsorption capacity of raw clay and modified clays under batch experiments. Various models were used to describe and examine the parameters of the kinetic and isotherm experiments. A simple and economic preparation of the iron modified natural common clays was performed. Plus, type of isotherms and thermodynamic parameters for the adsorption were also evaluated.

II. MATERIALS AND METHODS

A. Preparation of Adsorbents

Natural clays in this study were collected from

Manuscript received November 24, 2014; revised January 24, 2015. This work was supported in part by the School of Environmental Engineering, Suranaree University of Technology, Thailand.

Borano Te, Boonchai Wichitsathian, and Chatpet Yossapol are with the School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand (e-mail: te.borano@yahoo.com, boonchai@sut.ac.th, chatpet@sut.ac.th).

North-eastern part of Thailand (Dan Kwian District, Nakhon Ratchasima Province). The samples were cleaned with deionized water (DI water), dried at 104°C for 24 h, crushed with mortar and pestle and sieved to achieve the required particle size of less than 75 µm. The dried clean clays with the desirable particle size were labeled as Raw Clay adsorbent and kept in a dry and clean container for modification process. The modification process was conducted as the following. 20g of dried clean clays were added to 200 ml of 0.1M FeCl₃ 6H₂O or FeSO₄ 7H₂O solution in a capped 250 ml Erlenmeyer flask. The mixture was shaken on a mechanical shaker with agitation speed of 150 rpm at room temperature for 24 h. Then, the solid was separated from liquid by centrifugation at 3000 rpm for 5 min and dried at 105 °C for 24 h. The dried solid was further heated at moderate temperature (300 °C) in a muffle furnace for about 3 h. After cooling down, the particles were washed with DI water until no reddish color or precipitates upon addition of a few drops of 1:10-phenanthroline, and dried at 60°C overnight in a hot air flow oven. The final products were labeled as Clay/FeCl₃ and Clay/FeSO₄, respectively, and kept in dry and clean containers for further use.

B. Characterization of Adsorbents

The elemental composition of Raw Clay was analyzed by Energy Dispersive X-ray Fluorescence (ED-XRF) (XGT-5200 X-ray Analytical Microscope, HORIBA Ltd., Japan). The specific surface area, pore volume, and average pore diameter of the adsorbents were calculated from nitrogen adsorption-desorption isotherm data at 77 K by the Brunauer-Emmett-Teller (BET) methods using the BET analyzer (BELSORP Mini II, BEL Inc., Japan). Before determining the isotherms, the samples are outgassed by heating at 60°C for 24 h under N₂ flow by the pretreatment instrument (BELPREP-vacII, BEL Inc., Japan). The point of zero charge (pH_{pzc}) was evaluated by plotting the initial pH as a function of the equilibrium pH (Using 0.01M NaCl as background electrolyte with the equilibrium time of 24h) according to the method proposed by [20].

C. Reagents and Apparatus

All chemical reagents used in this study were analytical grade, which were purchased from Italmar Co., Ltd., Thailand. The stock solution of As(V) with concentration of 100 mg/L was prepared by dissolving sodium hydrogen arsenate (Na₂HAsO₄) (Sigma-Aldrich chemical) in ultrapure water (resistivity 18.2 M Ω) obtained with a Mili-Q water purification system. Arsenate concentrations with further appropriate dilutions were freshly made. Iron solutions for modification were prepared from ferric solution (FeCl₃ 6H₂O) and ferrous solution (FeSO₄ 7H₂O). To prevent chemical interferences, glassware and plastic bottles were washed with DI water and exposed to a 5% nitric acid solution overnight prior to being used. Adjustment of pH was done by means of a dilute HCl or NaOH solution.

D. Instrumentals

The analysis for arsenate concentration was done by inductively coupled plasma-optical emission spectrometry (ICP-OES) (Optima 8000, PerkinElmer, USA) at a wavelength 193.7 nm. The instrument was calibrated by using

various standard diluted arsenate stock solutions. The measurement of pH was made on a pH meter (Mettler Toledo, Switzerland).

E. Batch Adsorption Studies

Batch adsorption experiments were carried out at room temperature (25 ± 1°C) in acid washed 250 mL Erlenmeyer flasks or 50 mL centrifuge tubes. A certain volume of known concentration of As(V) was mixed with a certain amount of the adsorbents. The mixture was shaken at 150 rpm on a horizontal mechanical shaker (New Brunswick Scientific, Canada) for the equilibrium time. The supernatant was then filtered through 0.22 µm syringe filter. The filtrates were stored at 4°C until the time for arsenate analyzing by ICP-OES. Blanks (without addition of the adsorbents) were also run at the same condition to determine whether any measureable adsorption of As(V) occurred on the wall of the flasks or tubes. Each experiment was conducted in duplicate and the average of the measurements was calculated. The amount of As(V) adsorbed per unit mass of the adsorbents, q_e (mg/g), and the percentage of As(V) adsorbed, $A\%$, were computed respectively using following equations:

$$q_e = \left(\frac{C_o - C_e}{M} \right) V \quad (1)$$

$$A\% = \left(\frac{C_o - C_e}{C_o} \right) 100 \quad (2)$$

where C_o (mg/L) is the initial concentration of arsenate, C_e (mg/L) is the equilibrium concentration of arsenate, V (L) is the volume of the arsenate solution, and M (g) is the mass of adsorbents used in the experiments.

F. Effect of pH

The effect of pH for As(V) adsorption on the adsorbent was investigated by adjusting the pH value of the solution from 4 to 11. 40 mL of initial As(V) concentration of 10 mg/L and 5 g/L of the adsorbent were mixed in the 50 mL acid washed centrifuge tube. The tubes were shaken on the shaker at agitation speed of 150 rpm and room temperature (25 ± 1°C) for the equilibrium time.

G. Kinetic Experiments

Kinetic experiments were carried out in the acid washed 250 mL Erlenmeyer flasks with 200 mL of synthetic As(V) solution (10 mg/L) and 10 g/L of the adsorbent. During the adsorption, the supernatant samples were taken at fixed time intervals and filtered through 0.22 µm syringe filter to analyze for the arsenate concentration. The pseudo first and pseudo second order models were applied to determine the kinetic parameters. These models are represented by the linearized forms as the following:

Pseudo first order model:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (3)$$

Pseudo second order model:

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (4)$$

where q_e (mg/g) and q_t (mg/g) are the amount of As(V) adsorbed at equilibrium and at time t (h), respectively, and k_1 (h⁻¹) and k_2 (g mg⁻¹ h⁻¹) are pseudo first order and pseudo second order kinetic constants, respectively.

H. Isotherm Experiments

Isotherm experiments were conducted in 50 mL polyethylene centrifuge tubes with 10 g/L of the adsorbents and 40 mL of As(V) solution for the equilibrium time. The As(V) concentrations were 1, 5, 10, 20, 30, 40, and 50 mg/L. The supernatant samples were filtered through 0.22 μm syringe filter to analyze for the arsenate concentration in the filtrate. Langmuir and Freundlich adsorption models were used for isotherm modeling. These models can be expressed as:

Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (5)$$

Freundlich model:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (6)$$

where q_m (mg/g) is the maximum amount of As(V) adsorbed at equilibrium, K_L (L/mg) is the Langmuir constant, and K_f (mg¹⁻ⁿg⁻¹Lⁿ) and n are the Freundlich constants related to adsorption capacity and adsorption intensity of adsorbent, respectively.

I. Effect of Temperature

The effect of temperature for As(V) adsorption on the adsorbent was investigated in 250 mL Erlenmeyer flasks with 50 mL of synthetic As(V) solution (10 mg/L) and 10 g/L of the adsorbents. The flasks were shaken on the shaker at agitation speed of 150 rpm for the equilibrium time. The temperatures were 35, 45, 55, and 65°C. The thermodynamic parameters of the adsorption were calculated using the following equations:

$$\Delta G^0 = -RT \ln K_d \quad (7)$$

$$\ln K_d = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (8)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (9)$$

where ΔG^0 is the Gibbs free energy change (kJ/mol), ΔH^0 is the standard enthalpy change (kJ/mol), ΔS^0 is the standard entropy change (J/mol K), T is the absolute temperature (K), R is the universal gas constant (8.314 J/mol K). K_d (L/g) is the equilibrium constant defined by As(V) adsorbed at equilibrium (q_e) over As(V) concentration at equilibrium (C_e) [21].

III. RESULTS AND DISCUSSION

A. Properties of Adsorbent

The physical chemical properties of the adsorbents were presented in Table I. The chemical compositions of natural

common clay for further modification were: Al₂O₃ (25.26%), SiO₂ (66.86%), K₂O (1.48%), CaO (0.52%), TiO₂ (1.04%), MnO₂ (0.05%), and Fe₂O₃ (5.29%). The analysis revealed that the major constituents were SiO₂ and Al₂O₃, followed by Fe₂O₃. From the BET analysis, the surface area of Raw Clay, Clay/FeSO₄, and Clay/FeCl₃ were 52.45, 51.00, and 52.08m²/g, respectively. Clay/FeSO₄ had highest values of average pore diameter (6.25 nm), followed by Clay/FeCl₃ (6.14 nm). p*H*_{pzc} was 5.90, 4.20, and 4.40 for Raw Clay, Clay/FeSO₄, and Clay/FeCl₃, respectively.

TABLE I: PHYSICAL-CHEMICAL PROPERTIES OF THE ADSORBENTS

Properties	Raw Clay	Clay/FeSO ₄	Clay/FeCl ₃
Surface area, S _{BET} (m ² /g)	52.45	51.00	52.08
Total pore volume (cm ³ /g)	0.075	0.079	0.080
Mean pore diameter (nm)	5.76	6.25	6.14
Point of zero charge (p <i>H</i> _{pzc})	5.90	4.20	4.40

B. Effect of pH

Arsenate species and the surface charge of the adsorbent in aqueous solution are pH dependent, which make pH be one of the most important factors affecting arsenate adsorption onto the adsorbent in the liquid phase [22]. The effect of pH on arsenate adsorption onto raw clay and modified clays is shown in Fig. 1. It was found that arsenate adsorption onto all adsorbents was pH dependent and the maximum adsorption occurred at lower pH values. The adsorption efficiency for all adsorbents decreased with the increase of the initial pH, and sharply decreased when the initial pH is above 10.

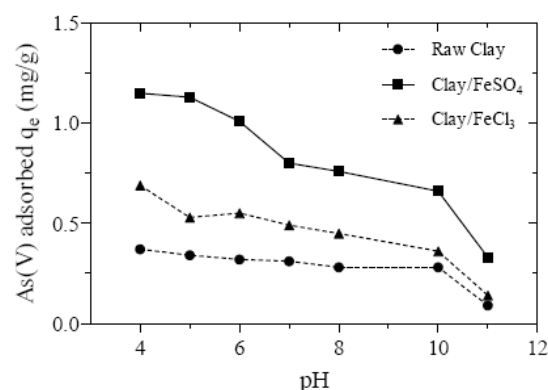


Fig. 1. Effect of pH on the As(V) adsorption onto Raw Clay, Clay/FeSO₄, and Clay/FeCl₃.

Arsenate species in aqueous phase exist mainly as H₃AsO₄ at pH less than 2.2, H₂AsO₄⁻ at pH between 2.2 and 6.98, HAsO₄²⁻ at pH between 6.98 and 11.5, and AsO₄³⁻ at pH above 11.5. The surface charge of the adsorbents becomes more positively charged when pH is less than p*H*_{pzc} and more negatively charged when pH is above p*H*_{pzc} [22]. A better performance of the adsorption occurred at acidic condition can be interpreted that the more positive charge of the adsorbents (p*H* < p*H*_{pzc}) provided more adsorption sites for the predominant arsenate species (H₂AsO₄⁻ or HAsO₄⁻). When pH increased to higher than p*H*_{pzc}, repulsive force between the adsorbents and the adsorbate has increased resulting in decreasing As(V) uptake from the solution. Therefore, pH values have impact on arsenate adsorption due to the change of the electrostatic force between arsenate species and the

adsorbents.

C. Kinetic Studies

The plots of the amount of As(V) adsorbed versus contact time are given in Fig. 2. The results showed that As(V) adsorption was fast within the first hour of agitation time and slow afterwards until equilibrium. The rapid uptake of As(V) within the first hour was due to the more presence of competent active adsorbing sites on the surface of the adsorbent at the initial stage of the contact time. Equilibrium time was achieved within 24h, and was used for other experiments.

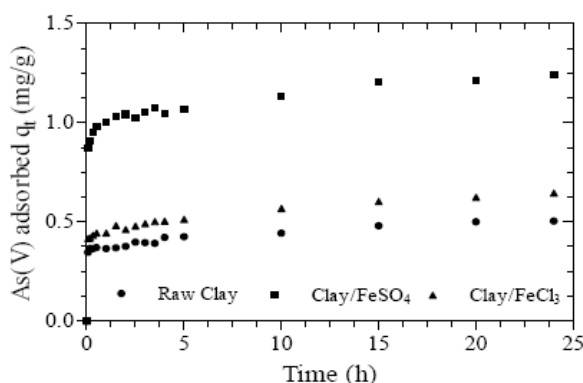


Fig. 2. Effect of contact time on the As(V) adsorption onto Raw Clay, Clay/FeSO₄, and Clay/FeCl₃.

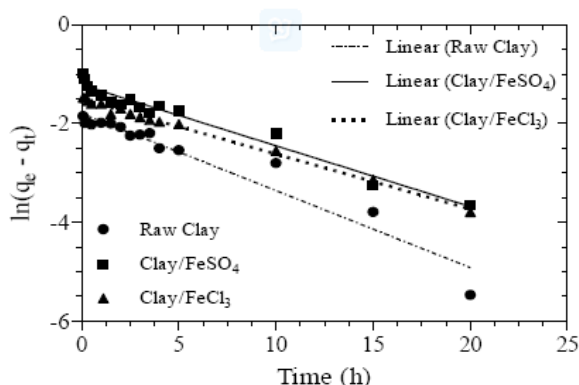


Fig. 3. Pseudo first order kinetics for the As(V) adsorption on Raw Clay, Clay/FeSO₄, and Clay/FeCl₃.

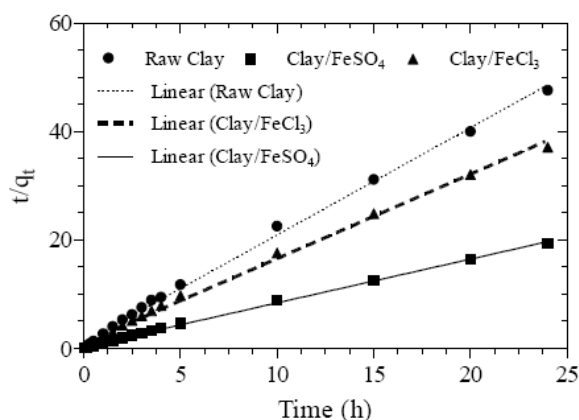


Fig. 4. Pseudo second order kinetics for the As(V) adsorption on Raw Clay, Clay/FeSO₄, and Clay/FeCl₃.

The kinetic data on arsenate adsorption to the adsorbents were modeled by the pseudo first order and the pseudo second order models. The rate constant (k_1) and calculated equilibrium capacity ($q_{e,cal}$) of the pseudo first order models

were determined from the plot of $\ln(q_e - q_t)$ versus t (Fig. 3). The rate constant (k_2) and calculated equilibrium capacity ($q_{e,cal}$) of the pseudo second order models were determined from the plot of t/q_t versus t (Fig. 4). Kinetic parameters of the pseudo first order and pseudo second order models are given in Table II.

The values of correlation coefficient (R^2) of the adsorbents (Raw Clay, Clay/FeSO₄ and Clay/FeCl₃ were 0.9298, 0.9698, and 0.9916, respectively) for the pseudo first order adsorption model are lower than those of the adsorbents (Raw Clay, Clay/FeSO₄ and Clay/FeCl₃ were 0.9969, 0.9987, and 0.9963, respectively) for the pseudo second order model.

TABLE II: KINETIC PARAMETERS FOR AS(V) ADSORPTION ON DIFFERENT ADSORBENTS

	Raw Clay	Clay/FeSO ₄	Clay/FeCl ₃
$q_{e,exp}$ (mg/g)	0.504	1.230	0.650
Pseudo first order			
$q_{e,cal}$ (mg/g)	0.170	0.306	0.221
k_1 (h ⁻¹)	0.1580	0.1609	0.1111
R^2	0.9298	0.9698	0.9916
Pseudo second order			
$q_{e,cal}$ (mg/g)	0.506	1.231	0.6422
k_2 (g.mg ⁻¹ .h ⁻¹)	3.4730	2.2140	2.4820
R^2	0.9969	0.9987	0.9963

Additionally, theoretical or experimental values ($q_{e,exp}$) of the adsorbents (Raw Clay, Clay/FeSO₄ and Clay/FeCl₃ were 0.504, 1.230, and 0.650 mg/g, respectively) obtained from the pseudo second order are in a good accordance with the calculated equilibrium adsorption capacity ($q_{e,cal}$) of the adsorbents (Raw Clay, Clay/FeSO₄ and Clay/FeCl₃ were 0.506, 1.231, and 0.642 mg/g, respectively). Therefore, the arsenate adsorption onto the studied adsorbents followed the pseudo second order adsorption model.

D. Isotherm Studies

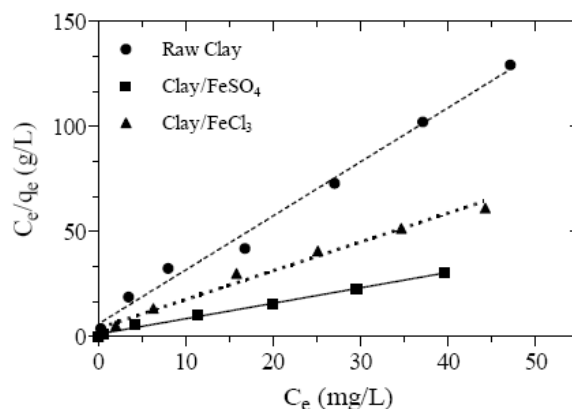


Fig. 5. Langmuir plot for the As(V) adsorption on Raw Clay, Clay/FeSO₄, and Clay/FeCl₃.

The Langmuir and Freundlich models were used to analyze the isotherm data. For the Langmuir model, q_m (mg/g) and K_L (L/mg) were computed from the slope and intercept of the plot C_e/q_e versus C_e , respectively (Fig. 5). For the Freundlich model, $1/n$ and K_f (mg¹⁻ⁿ.g⁻¹.Lⁿ) were obtained from the slope and intercept of the plot $\ln q_e$ and $\ln C_e$, respectively (Fig. 6). Values of the isotherm parameters are presented in Table III. Raw Clay and Clay/FeSO₄ were well described by the

Langmuir model with correlation coefficients (R^2) 0.9903 and 0.9932, respectively. Clay/ FeCl_3 was fitted well to the Freundlich model with correlation coefficient (R^2) 0.9922. The estimated maximum adsorption capacity was 0.44, 1.50, and 0.86 mg/g for Raw Clay, Clay/ FeSO_4 , and Clay/ FeCl_3 , respectively. The nature of adsorption isotherm can be predicted by evaluating the essential characteristic of the Langmuir isotherm expressed in terms of a dimensionless constant separation factor, R_L . The separation factor was computed by $R_L = 1/(1 + K_L C_o)$, where C_o (mg/L) is the initial As(V) concentration.

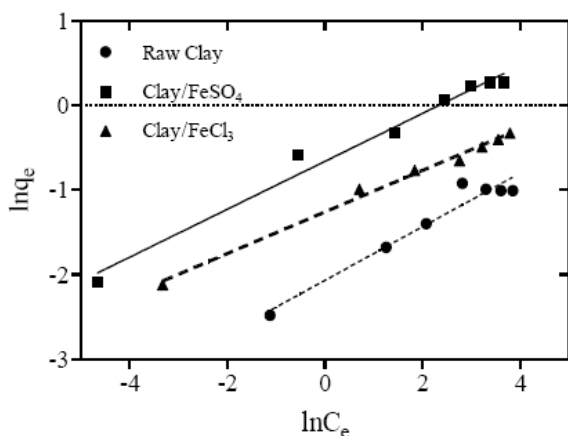


Fig. 6. Freundlich plot for the As(V) adsorption on Raw Clay, Clay/ FeSO_4 , and Clay/ FeCl_3 .

TABLE III: CALCULATED ADSORPTION ISOTHERM PARAMETERS

Model	Raw Clay	Clay/ FeSO_4	Clay/ FeCl_3
Langmuir			
q_m (mg/g)	0.44	1.50	0.86
K_L (Lmg $^{-1}$)	0.3830	0.5210	0.2946
R_L	0.05-0.72	0.04-0.66	0.06-0.77
R^2	0.9903	0.9932	0.9835
Freundlich			
K_f	0.1126	0.5150	0.2800
$1/n$	0.32	0.28	0.25
R^2	0.9728	0.9806	0.9922

The adsorption process is irreversible if $R_L=0$, favorable if $0 < R_L < 1$, linear if $R_L=1$ and unfavorable if $R_L=1$ [15]. The values of R_L computed for As(V) adsorption on Raw Clay, Clay/ FeSO_4 , and Clay/ FeCl_3 were 0.05-0.72, 0.04-0.66, and 0.06-0.77, respectively. The obtained values of R_L are within the range of 0-1, which indicated that the favorable equilibrium As(V) adsorption occurred for all adsorbents. Similarly, the magnitude of the adsorption intensity, $1/n$, can suggest the type of isotherm from the Freundlich model. The adsorption is favorable when $0 < 1/n < 1$, irreversible when $1/n=1$ and unfavorable when $1/n > 1$ [1]. The values of $1/n$ obtained from the equilibrium adsorption of As(V) were 0.32, 0.28, and 0.25 for Raw Clay, Clay/ FeSO_4 , and Clay/ FeCl_3 , respectively, which fell within the range of 0-1. Therefore, As(V) was adsorbed favorably on all adsorbents.

E. Thermodynamic Parameters

The equilibrium constant values, K_d , for As(V) adsorption on the adsorbent were calculated at different temperatures (308, 318, 328, and 338 K) by dividing q_e with C_e . These values were used to calculate the thermodynamic parameters.

The ΔH° value was determined from the slope of the linear plot of $\ln K_d$ versus $1/T$, as shown in Fig. 7. The values of thermodynamic parameters for the adsorption of As(V) were presented in Table IV. Gibbs free energy change (ΔG°) was found to be negative in values while both standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were found to be positive. References [21]-[24] suggested that the negative values of ΔG° and the positive of ΔH° indicate the adsorption is spontaneous and endothermic, and positive ΔS° value of the adsorption process indicates an increase of the randomness at the adsorbent-adsorbate interface during the adsorption.

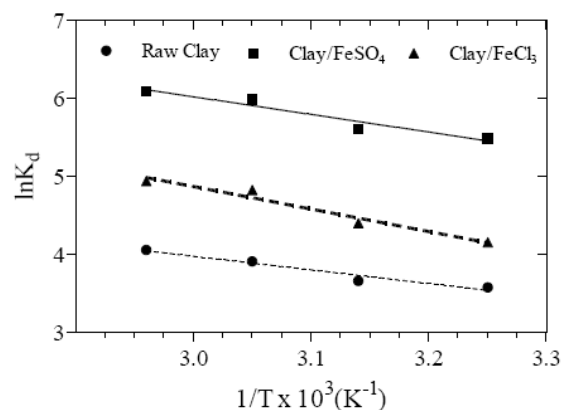


Fig. 7. The plot of $\ln K_d$ versus $1/T$ for the As(V) adsorption on Raw Clay, Clay/ FeSO_4 , and Clay/ FeCl_3 .

TABLE IV: THERMODYNAMIC PARAMETERS FOR THE A(V) ADSORPTION ONTO RAW CLAY AND MODIFIED CLAY ADSORBENTS

T(K)	$\ln K_d$	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/molK)
Raw Clay				
308	3.58	-9.16	+14.48	+76.78
318	3.66	-9.68		+75.99
328	3.91	-10.67		+76.68
338	4.06	-11.40		+76.59
Clay/ FeSO_4				
308	5.49	-14.05	+18.75	+106.50
318	5.61	-14.85		+105.64
328	5.99	-16.34		+106.97
338	6.09	-17.12		+106.14
Clay/ FeCl_3				
308	4.16	-10.64	+23.95	+112.32
318	4.40	-11.64		+111.93
328	4.83	-13.17		+113.18
338	4.94	-13.87		+111.91

IV. CONCLUSION

Natural common clays, low cost materials and widely available, can be modified with ferric and ferrous solutions to be the adsorbents for arsenate removal from water. The modification is cheap and simple process. Compared with raw clay's arsenate uptake, iron modification process has effect on the arsenate adsorption efficiency from a synthetic aqueous solution. The ferric solution has increased the uptake efficiency two times, and the ferrous solution has increased efficiency three folds. Arsenate adsorption by modified adsorbents, both Clay/ FeSO_4 and Clay/ FeCl_3 , is affected by pH values of the solution. Therefore, natural clays can be used to support iron species solutions to be low cost and more

efficient adsorbents for arsenate removal from water. However, further studies should be considered before the adsorbents can be applied in the arsenic contaminated areas to supply safe drinking water. The studies may involve the effect of various minerals (Chloride, sulfate, phosphate, which are mostly found in the natural water), and the performance of the adsorbents in the column.

ACKNOWLEDGMENT

This study was supported by SUT-ASEAN Scholarship program, the Center for Scientific and Technological Equipment, and School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand.

REFERENCES

- [1] F. Fufa, E. Alemayehu, and B. Lennartz, "Sorption removal of arsenate using termite mound," *J. Environ. Manage.*, vol. 132, pp. 188-196, 2014.
- [2] A. K. Sharma, J. C. Tjell, J. J. Sloth, and P. E. Holm, "Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas," *Applied Geochemistry*, vol. 41, pp. 11-33, 2014.
- [3] Y. Chen, F. Parvez, M. Gamble, T. Islam, A. Ahmed, M. Argos, J. H. Graziano, and H. Ahsan, "Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: Review of recent findings from the health effects of arsenic longitudinal study (HEALS) in Bangladesh," *Toxicol. Appl. Pharmacol.*, vol. 239, pp. 184-192, 2009.
- [4] H. Brammer and P. Ravenscroft, "Arsenic in groundwater: a threat to sustainable agriculture in South and South-east Asia," *Environ. Int.*, vol. 35, pp. 647-654, 2009.
- [5] S. Luther, N. Borgfeld, J. Kim, and J. G. Parsons, "Removal of arsenic from aqueous solution: A study of the effects of pH and interfering ions using iron oxide nanomaterials," *Microchemical Journal*, vol. 101, pp. 30-36, 2012.
- [6] D. Masih, Y. Izumi, K. Aika, and Y. Seida, "Optimization of an iron intercalated montmorillonite preparation for the removal of arsenic at low concentrations," *Engineering in Life Sciences*, vol. 7, pp. 52-60, 2007.
- [7] I. Villaescusa and J. C. Bollinger, "Arsenic in drinking water: sources, occurrence and health effects (a review)," *Reviews in Environmental Science and Bio/Technology*, vol. 7, pp. 307-323, 2008.
- [8] S. Wang and C. N. Mulligan, "Occurrence of arsenic contamination in Canada: sources, behavior and distribution," *Sci. Total Environ.*, vol. 366, pp. 701-721, 2006.
- [9] P. Mondal, S. Bhowmick, D. Chatterjee, A. Figoli, and B. Van der Bruggen, "Remediation of inorganic arsenic in groundwater for safe water supply: A critical assessment of technological solutions," *Chemosphere*, vol. 92, pp. 157-170, 2013.
- [10] A. V. Vitela-Rodriguez and J. R. Rangel-Mendez, "Arsenic removal by modified activated carbons with iron hydro(oxide) nanoparticles," *J. Environ. Manage.*, vol. 114, pp. 225-231, 2013.
- [11] P. Sabbatini, F. Yrazu, F. Rossi, G. Thern, A. Marajofsky, and M. M. F. de Cortalezzi, "Fabrication and characterization of iron oxide ceramic membranes for arsenic removal," *Water Res.*, vol. 44, pp. 5702-12, 2010.
- [12] B. Dousova, T. Grygar, A. Martaus, L. Fuitova, D. Kolousek, and V. Machovic, "Sorption of As(V) on aluminosilicates treated with Fe(II) nanoparticles," *J. Colloid. Interface Sci.*, vol. 302, pp. 424-431, 2006.
- [13] A. Zehhaf, A. Benyoucef, C. Quijada, S. Taleb, and E. Morallón, "Algerian natural montmorillonites for arsenic(III) removal in aqueous solution," *International Journal of Environmental Science and Technology*, 2013.
- [14] A. Ramesh, H. Hasegawa, T. Maki, and K. Ueda, "Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite," *Separation and Purification Technology*, vol. 56, pp. 90-100, 2007.
- [15] A. Sdiri, T. Higashi, T. Hatta, F. Jamoussi, and N. Tase, "Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems," *Chemical Engineering Journal*, vol. 172, pp. 37-46, 2011.
- [16] X. Ren, Z. Zhang, H. Luo, B. Hu, Z. Dang, C. Yang, and L. Li, "Adsorption of arsenic on modified montmorillonite," *Applied Clay Science*, vol. 97-98, pp. 17-23, 2014.
- [17] C. Luengo, V. Puccia, and M. Avena, "Arsenate adsorption and desorption kinetics on a Fe(III)-modified montmorillonite," *J. Hazard Mater.*, vol. 186, pp. 1713-1719, 2011.
- [18] M. Q. Jiang, Q. P. Wang, X. Y. Jin, and Z. L. Chen, "Removal of Pb(II) from aqueous solution using modified and unmodified kaolinite clay," *J. Hazard Mater.*, vol. 170, pp. 332-339, 2009.
- [19] D. Mohapatra, D. Mishra, G. R. Chaudhury, and R. P. Das, "Arsenic(V) adsorption mechanism using kaolinite, montmorillonite and illite from aqueous medium," *J. Environ. Sci. Health A Tox Hazard Subst. Environ. Eng.*, vol. 42, pp. 463-469, 2007.
- [20] J. Su, H. G. Huang, X. Y. Jin, X. Q. Lu, and Z. L. Chen, "Synthesis, characterization and kinetic of a surfactant-modified bentonite used to remove As(III) and As(V) from aqueous solution," *J. Hazard Mater.*, vol. 185, pp. 63-70, 2011.
- [21] S. M. Al-Rashed and A. A. Al-Gaid, "Kinetic and thermodynamic studies on the adsorption behavior of Rhodamine B dye on Duolite C-20 resin," *Journal of Saudi Chemical Society*, vol. 16, pp. 209-215, 2012.
- [22] Q. Chang, W. Lin, and W. C. Ying, "Preparation of iron-impregnated granular activated carbon for arsenic removal from drinking water," *J. Hazard Mater.*, vol. 184, pp. 515-522, 2010.
- [23] T. Sumathi and G. Alagumuthu, "Adsorption Studies for Arsenic Removal Using Activated Moringa oleifera," *International Journal of Chemical Engineering*, vol. 2014, pp. 1-6, 2014.
- [24] F. Zha, W. Huang, J. Wang, Y. Chang, J. Ding, and J. Ma, "Kinetic and thermodynamic aspects of arsenate adsorption on aluminum oxide modified palygorskite nanocomposites," *Chemical Engineering Journal*, vol. 215-216, pp. 579-585, 2013.



Borano Te was born in Kampong Cham, Cambodia on December 12, 1987. He obtained a bachelor degree of technology in civil construction from Preah Kossamak Polytechnic Institute, Phnom Penh, Cambodia in 2008. In 2010, he graduated with a bachelor degree of science in environmental science from Pannasastra University of Cambodia, Phnom Penh, Cambodia. In 2012, he won a SUT-ASEAN PhD Scholarship program to pursue a graduate study at Suranaree University of Technology (SUT), Nakhon Ratchasima, Thailand. Now, he is a PhD student at SUT. His research interest is the arsenic removal from aqueous solution using clays and modified clays.



Boonchai Wichitsathian was born in Bangkok, Thailand. He obtained a bachelor degree of industrial chemistry and a master degree of environmental technology from King Mongkut's Institute of Technology Thonburi (KMUTT), Bangkok, Thailand. He earned his degree of doctor of technical science in environmental technology and management from Asian Institute of Technology (AIT) under scholarship of Royal Thai Government. Now, he is a lecturer in the School of Environmental Engineering, and a director of the Center for Cooperative Education and Career Development, Suranaree University of Technology, Thailand.



Chatpet Yassopol was born in Nakhon Ratchasima, Thailand. He received his bachelor degree of engineering in environmental engineering from Khon Kaen University, Thailand and master degree of engineering in environmental engineering from Chulalongkorn University, Bangkok, Thailand. He earned his Ph.D. degree in environmental engineering from New Jersey Institute of Technology, USA. In the present, he holds a position as a lecturer in the School of Environmental Engineering, as a deputy director of the Center of Scientific and Technological Equipment, and as the head of Suranaree Environmental Technology Research and Consulting Unit, Suranaree University of Technology, Thailand.