Adsorption of Arsenate on Clays

Sumrit Mopoung* and Prasak Thavornyutikarn**,

*Naresuan University, Thailand
**Chiang Mai University, Thailand

ABSTRACT

The adsorption of arsenate by four adsorbents; Mae Rim Clay (Mae Rim), Yellow Clay (Hang Dong), Red Clay (Doi Saket) and Laterite (Pa Sang) (Thailand) were studied. The rate of arsenic adsorption from solution by four adsorbents are rapid for the first few hour and then approach equilibrium within 24 hours at 100 mg L^{-1} initial arsenate concentration. The amount of arsenate adsorbed increases with increasing pH and reaches a maximum at pH 5 for Mae Rim Clay and Red Clay, at pH 7 for Yellow Clay and at pH 6 for Laterite, then decreased afterward when the arsenate concentration range from 50 to 200 mg L^{-1}. The Freundlich isotherm equation was successfully used to describe arsenate adsorption over an initial concentration range of 25 to 200 mg L^{-1} arsenate for all adsorbents. The arsenate sorption capacity of adsorbents increased in the order: Mae Rim Clay < Yellow Clay < Laterite < Red Clay at pH 4 and 9, but increased in the order: Mae Rim Clay < Laterite < Red Clay < Yellow Clay at pH 7.

Keywords: arsenate / adsorption / adsorption isotherm / adsorbent / equilibration time

INTRODUCTION

The most probable oxidation states of arsenic in soil environments are +3 and +5, although the –3 and 0 oxidation states are also possible in strongly reduced soils and sediments. Arsenate (as $H_2AsO_4^-$ and $HAsO_4^{2-}$) is the predominant arsenic form in oxidized environments (Masscheleyn et al. 1991). Arsenate, $H_2AsO_4^-$ species are predominant within the pH 2.0-7.0, and above this range, $HAsO_4^{2-}$ species are dominant up to pH 12.0 (Singh et al. 1996). The availability of arsenic to plants and its movement in soils to ground waters is dependent not on the total arsenic concentration of a site, but on the soluble fraction of arsenic present. Methods that are able to permanently reduce the mobility of arsenic in contaminated soils will in turn reduce the toxicity and pollution potential of such soils (Jain et al. 1999).

The work proposed here will examine and compare the ability of a number of clays [Mae Rim Clay (Mae Rim District, Chiang Mai Province), Yellow Clay (Hang Dong District, Chiang Mai Province), Red Clay (Doi Saket Distric, Chiang Mai Province), and Laterite (Pa Sang Distric, Lamphun Province), Thailand] for the reduction of arsenate solubility by "locking it up" as a permanent compound.

MATERIALS AND METHODS

Mae Rim Clay, Yellow Clay, Red Clay, Laterite were used in the investigation. The Mae Rim Clay, Yellow Clay, Red Clay, and Laterite were air-

dried, then crushed and passed through a –80 mesh sieve. A number of physical and chemical properties of these clays were measured by standard methods and are listed in Table 1. XRF spectrometer (Philips PW 1404 and PW 1480) is used to analyze the composition of Clays. Arsenic was measured by inductive coupled plasma mass spectrometer (Perkin Elmer Elan 6000). Clay pH was determinded in a 1:1 clay:water suspension (Jackson 1965). The pH at the zero point of charge (pH_{ZPC}) was determined by method of Pierce and Moore (1980). The surface area was measured by using a gravimetric BET N_2 adsorption technique (Quantachrome). Particle size distribution was measured using wet-sieving method (Black et al. 1986). The type of mineral was characterized by X-ray diffractometer (PW 3040/60, X' Pert Pro MPD).

Each adsorbents were aged with deionized water for one week before all experiments to ensure complete hydration. Three replicates were run for each experiment.

Determination of Equilibration Time

Equilibrium time was studied using the method of Pierce and Moore (1980). These studies were performed using an initial concentration of 100 mg L^{-1} arsenate [$Na_2HAsO_4.7H_2O$] to determine when equilibrium was reached. The adsorptions of arsenate were run at a constant concentration of each adsorbent (40 g L^{-1} weight by volume, w v^{-1}) and an ionic strength of 0.05 M NaCl in plastic bottles. Three replicate experiments for each adsorbent were run at solution pH's of 4.00, 7.00, and 9.00 (±0.05). The initial pH values were adjusted using either 1 M HCl or 1 M NaOH. The suspensions were placed in a water bath at 25°C. Samples were collected at various time intervals and the suspension was centrifuged at 16000 round min^{-1} (31000 g) for 10 minutes in a temperature controlled centrifuge (25± 1°C), then decanted for analyses. The concentration of arsenate was measured by colourimetry with molybdenum blue (Johnson and Pilson 1972).

The Adsorption Experiments

The adsorption experiments were carried out using the method of Pierce and Moore (1980). These experiments were performed using a constant concentration of the four adsorbents (2.00 g adsorbent per 50 mL, w v^{-1}) and an ionic strength of 0.05 M NaCl. Three initial arsenate concentrations in the form of $Na_2HAsO_4.7H_2O$ were used (50 mg L^{-1}, 100 mg L^{-1}, and 200 mg L^{-1}). The initial pH value of each solution was adjusted to give the desired final equilibrium pH between 3.00 and 10.00(±0.05). The initial pH values were adjusted using either 1 M HCl or 1 M NaOH to give the same final pH for each of the three different initial arsenate concentrations. The suspensions were mixed and placed in a water bath at 25±1°C for 48 hours. The pH values were adjusted each day to give the desired pH. At the end of the reaction period, the suspensions were centrifuged at 16000 round min^{-1} for 10 minutes in a temperature controlled centrifuge (25±1°C). The concentration of arsenate was measured by UV/VIS spectrophotometry.

A blank experiment was run without the adsorbent to see if arsenate adsorbed onto the walls of the bottles and centrifuge tubes.

The Adsorption Isotherm Experiments

Adsorption isotherms were determined using the method of Raven et al. (1998). These experiments were carried out at pH 4.00, 7.00 and 9.00 (±0.05) at initial arsenate solution concentrations of 25, 50, 100, 150 and 200 mg L^{-1}. The experimental set up was the same as for the adsorption studies. The pH of the adsorbent suspension was adjusted to the desired pH after addition of the arsenate solution and NaCl. The pH of the suspension was readjusted each day. After 48 hours the suspension was then centrifuged. The concentration of arsenate was measured by UV-VIS spectrophotometry.

The adherence of the adsorption data to Freundlich equations was tested graphically.

Table 1 Chemical constituents and physical properties of the adsorbents.

Constituents	Mae Rim Clay	Yellow Clay	Red Clay	Laterite
SiO_2 % w w^{-1}	53.50	46.74	32.90	30.53
Fe_2O_3 % w w^{-1}	1.39	4.02	24.80	19.62
P_2O_5 % w w^{-1}	0.01	0.05	0.12	0.33
Al_2O_3 %w w^{-1}	16.47	14.70	23.10	16.06
CaO % w w^{-1}	0.38	0.45	0.06	0.07
Na_2O %w w^{-1}	0.20	0.08	0.05	0.10
K_2O % w w^{-1}	3.17	3.52	0.12	1.13
MgO % w w^{-1}	0.01	0.03	0.33	0.02
MnO % w w^{-1}	0.01	0.02	0.12	4.13
Total As mg kg^{-1}	6.3	23.4	1.1	29.5
pH 1:1	5.54	7.61	4.86	8.50
pH_{ZPC}	5.30	7.60	5.10	6.6
% cumulative retain				
< 45μm	68.22	65.21	70.30	38.59
45-850 μm	31.41	34.64	29.70	61.32
> 850 μm	0.37	0.15	0.00	0.09
Surface area				
Multiple point BET, m^2 g^{-1}	23.18	30.11	52.63	42.97
Main type of mineral	Iron oxide Orthoclase Quartz	Siderite Muscovite Quartz	Hematite Kaolinite Quartz	Hematite Muscovite Quartz

w w^{-1} = weight by weight

RESULTS AND DISCUSSION

Adsorption Kinetics

Figure 1 show the adsorption kinetic of arsenate by Mae Rim Clay, Yellow Clay, Red Clay, and Laterite as a function of contact time for an initial concentration 100 mg L^{-1} in solution at pH 4.00, 7.00, and 9.00 ($\pm$ 0.05) and at temperature 25 ± 1°C. The arsenate adsorption is rapid during the first few hours and then approaches equilibrium after 5 hours at pH 4 and 6 hours at pH 7 and 9 for Mae Rim Clay, 5 hours at pH 4 and 7 and 6 hours at pH 9 for Yellow Clay, 4 hours at pH 4 and 5 hours at pH 7 and 9 for Red Clay and Laterite. From Figure 1, it can be seen that the adsorption of arsenate decreases with increasing pH from 4 to 9 for Mae Rim Clay, Red Clay, and Laterite. But for Yellow Clay, the adsorption of arsenate is highest at pH 7 and lowest at pH 9, respectively. These results are in good agreement with the findings of previous workers (Singh et al. 1996). Among the specie of arsenate are predominant within the pH 2.0–7.0 and pH 11.0 [Raven et al. 1998; Manning and Goldberg 1997). So that at low pH, the arsenate, which has a higher net negative charge, is adsorbed by positively charged surfaces quickly. But at high pH, $HAsO_4^{2-}$, is repulsed by negatively charged surfaces. Arsenate adsorption by Red Clay and Laterite was achieved quicter than with Mae Rim Clay and Yellow Clay. This may be attributed to the content of iron oxide, which are higher in Red Clay and Laterite. The iron oxides are highly effective in adsorption (Livesey and Huang 1981; Mariner et al. 1996).

Arsenate Adsorption

Figures 2 show that the arsenate adsorptions by four adsorbents are pH dependent and dependent on the initial concentration of arsenate in solution. The amount of arsenate adsorbed increased with a rise of pH upto a maximum at pH 5 for Mae Rim Clay and Red Clay, pH 7 for Yellow Clay, and pH 6 for Laterite and then generally decreased. It is note worthy that a significant amount of adsorption took place beyond the pH_{ZPC} of each adsorbent. The adsorption of arsenate will be favored electrostatically up to the pH_{ZPC} of the adsorbents but beyond this point specific adsorption plays an important role (Singh et al. 1996). The decrease in the extent of adsorption below the pH_{ZPC} of adsorbents may be attributed to the dissolution of the adsorbents and a consequent decrease in the number of adsorption sites (Singh et al. 1996). The lower adsorption of arsenate at high pH values is attributable to an increased repulsion between the more negative charged arsenate species ($HAsO_4^{2-}$) and negatively charged surface sites. Further, it may be seen that the adsorption of arsenate increases with increases in the initial concentration of arsenate from 50 to 200 mg L^{-1}. For example, the arsenate adsorption increases from 12.72 to 38.98 mmol arsenate kg^{-1} Mae Rim Clay at pH 5, from 13.64 to 42.63 mmol arsenate kg^{-1} Yellow Clay at pH 7, from 15.39 to 48.66 mmol arseanate kg^{-1} Red Clay at pH 5, and from 15.48 to 48.52 mmol arsenate kg^{-1} Laterite at pH 6. This may be attributed to lack of saturation over these concentration ranges (Wilkie and Hering 1996). Application of the surface complexation model to adsorption implies that the concentrations of surface binding sites available to adsorb adsorbate is

proportional to the amount of adsorbent and that the surface binding sites can become saturated at high adsorbate concentrations. However, at initial arsenate concentrations that are small compared with the concentrations of surface binding sites of the adsorbents, no surface saturation effects are expected. From Figures 2, it was seen that the arsenate sorption capacity of adsorbents increased in the order: Mae Rim Clay < Yellow Clay < Laterite < Red Clay at pH 4 and 9. This may be attributed to the content and type of mineral of iron oxide and aluminium oxide in adsorbents which are Hematite and Kaolinite(Table 1). But at pH 7, the arsenate sorption capacity of adsorbents increased in the order: Mae Rim Clay < Laterite < Red Clay < Yellow Clay at pH 7. This may be attributed to the effect of pH_{ZPC} of each adsorbents.

Adsorption Isotherm

The results obtained for the adsorption isotherms of arsenate. It was showed that the Freundlich equation was successfully used to describe arsenate adsorption over an initial concentration range of 25 to 200 mg L^{-1} arsenate for all adsorbents. The Freundlich isotherm for all adsorbents are shown in Figure 3. The R^2 values relating log x/m to log C were highly significant in all cases. It was clear that the composition of each adsorbents contains many types of oxides and oxide minerals. Oxides and oxide minerals are covered with the hydroxyl group in the aqueous environments. The Freundlich constants K and n were evaluated empirically for all adsorbents. These constants and the coefficients of determination (R^2) for the relationship between log x/m and log C are shown in Table 2. The Freundlich K value can be used for comparing the sorption capacity of the adsorbents (Elkhatip et al. 1984). The Freundlich K value decreases with increasing pH for the Mae Rim Clay, Red Clay, and Laterite. For the Yellow Clay, the Freundlich K value was higher at pH 7 than at pH 4 and 9. It was shown that the arsenate sorption capacity of the adsorbents increase in the order: Mae Rim < Yellow Clay < Laterite < Red Clay at pH 4 and 9, but increase in the order: Mae Rim Clay < Laterite < Red Clay < Yellow Clay at pH 7. The Freundlich K value for Yellow Clay was highest at pH 7. It may be attributed to the pH_{ZPC} of Yellow Clay (7.60). The Freundlich K value for Red Clay is the highest at pH 4 and 9. This may be attributed to the content iron oxide and particle size distribution (70.30 cumulative percent retain <45μm). The surface areas of soils increased with increasing contents of iron/aluminum oxide (Elkhatip et al. 1984; Goldberg and Glaubig 1988) and decreasing of particle size (Singh et al. 1996 and Prasad 1994). The values of n for arsenate adsorption on all adsorbents were >1, indicating a relatively high affinity of the arsenate for the sorption sites (Pusimo et al. 1997). Based on the Freundlich isotherm, it was concluded that the capture mechanism of arsenate proceeds by means of an irreversible chemical reaction (Elkhatip et al. 1984).
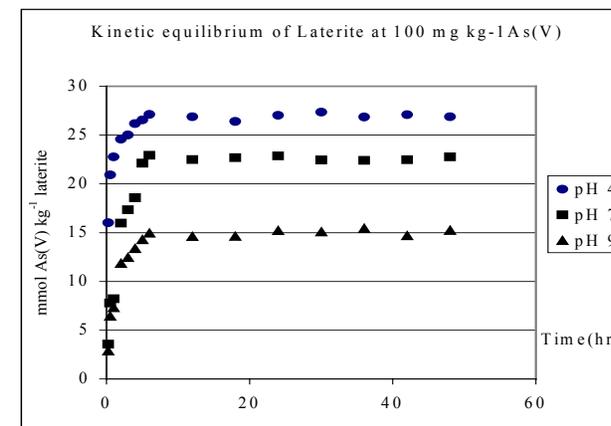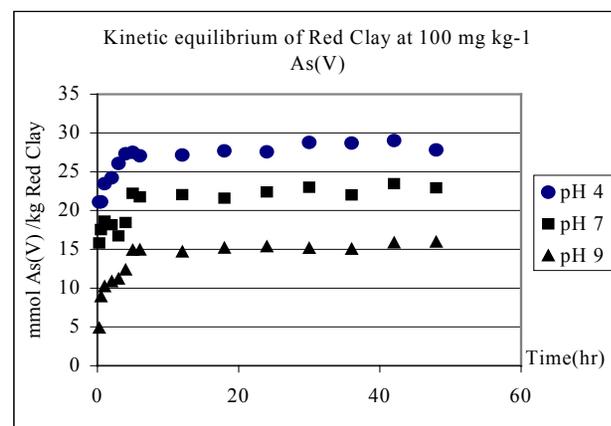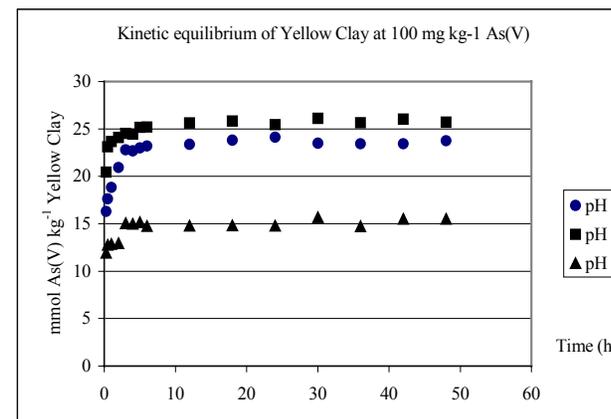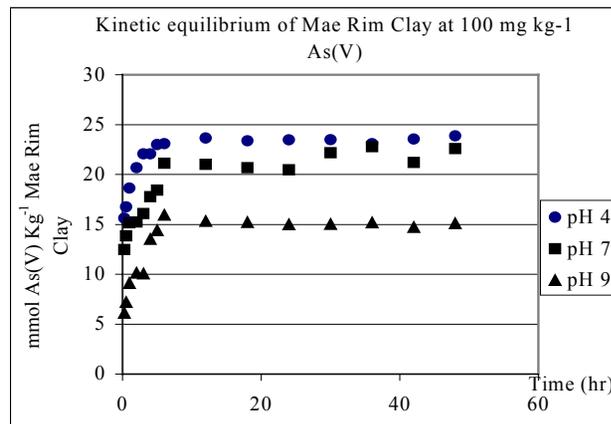
Figure 1 Kinetic equilibrium of adsorbents at initial concentration of 100 mg kg^{-1} arsenate [As(V)]
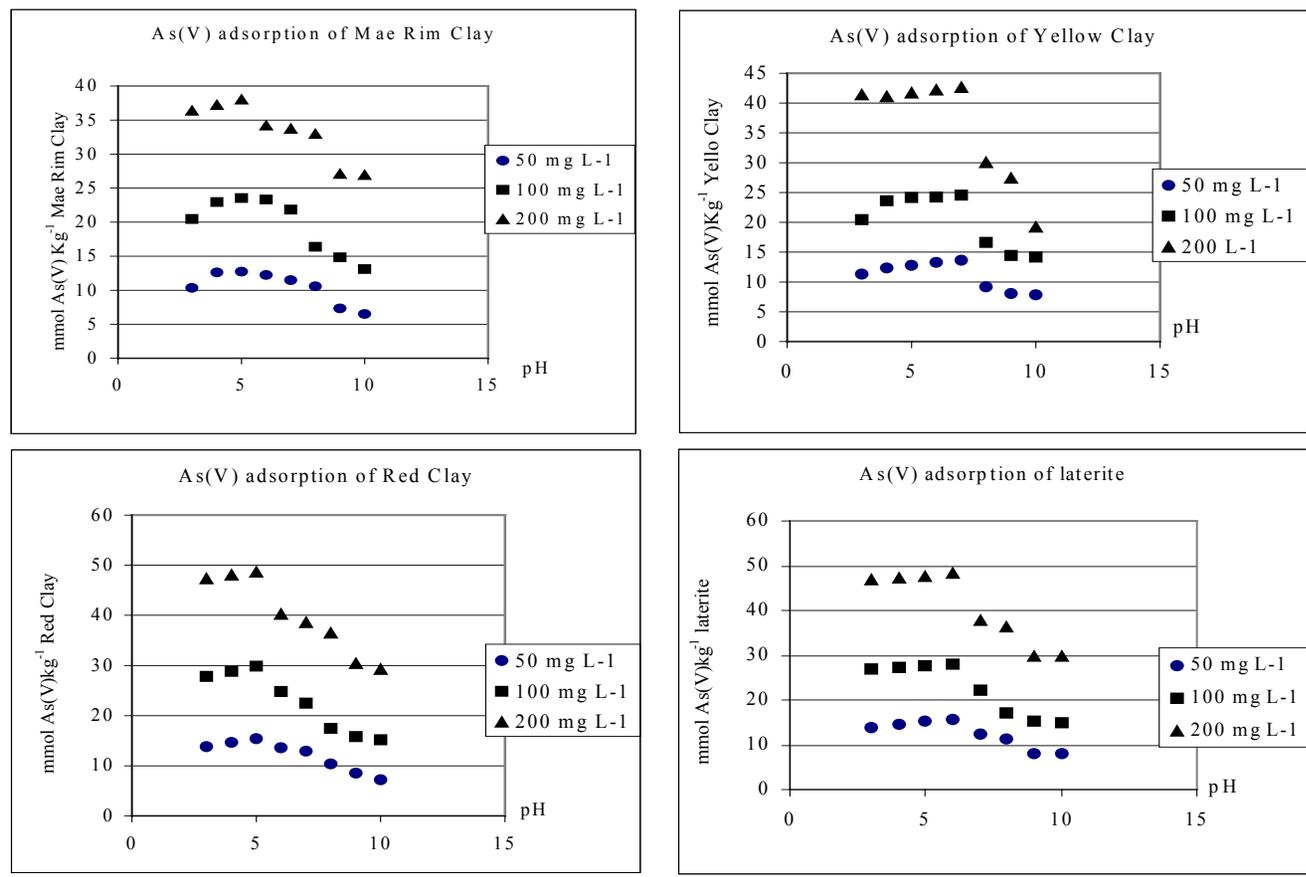
Figure 2 Arsenate adsorption by four adsorbents

As(V) adsorption Freundlich isotherm of Mae Rim Clay

$y = 0.5323x + 2.4282$
$R^2 = 0.9956$

$y = 0.8749x + 1.5673$
$R^2 = 0.9958$

$y = 0.6153x + 2.2339$
$R^2 = 0.9942$

- pH 4
- pH 7
- pH 9

log x/m

log C

Arsenate adsorption Freundlich isotherm of Yellow Clay

$y = 0.5499x + 2.5258$
$R^2 = 0.9923$

$y = 0.6886x + 1.9026$
$R^2 = 0.9962$

$y = 0.581x + 2.433$
$R^2 = 0.9892$

- pH 4
- pH 7
- pH 9

log x/m

log C

Arsenate adsorption Freundlich isotherm of Red Clay

$y = 0.5222x + 2.6541$
$R^2 = 0.9763$

$y = 0.5946x + 2.3359$
$R^2 = 0.9892$

$y = 0.5907x + 2.1417$
$R^2 = 0.9491$

- pH4
- pH 7
- pH 9

log x/m

log C

Arsenate adsorption Freundlich isotherm of Laterite

$y = 0.5695x + 2.5661$
$R^2 = 0.9783$

$y = 0.6026x + 2.3138$
$R^2 = 0.9945$

$y = 0.7002x + 1.9215$
$R^2 = 0.9753$

- pH 4
- pH 7
- pH 9

log x/m

log C

Figure 3 Arsenate adsorption Freundlich isotherm of adsorbents

Table 2 Freundlich parameters for the adsorption of arsenate of four adsorbents at pH 4.00, 7.00, and 9.00

	pH								
	4			7			9		
Adsorbents	K	n	R^2	K	n	R^2	K	n	R^2
Mae Rim Clay	268.04	1.879	0.9956	171.36	1.625	0.9942	36.92	1.143	0.9958
Yellow Clay	271.02	1.721	0.9892	335.58	1.819	0.9923	79.91	1.452	0.9962
Red Clay	450.92	1.915	0.9763	216.72	1.682	0.9892	138.58	1.693	0.9491
Laterite	368.21	1.756	0.9783	205.97	1.659	0.9945	83.46	1.428	0.9753

CONCLUSIONS

The amount of arsenate adsorption increases with rise of pH reaching a maximum for Mae Rim Clay and Red Clay at pH 5, for Yellow Clay at pH 7, and for Laterite at pH 6 then generally decreases. The Freundlich equation was successfully used to describe arsenate adsorption over an initial concentration range of 25 to 200 mg L^{-1} arsenate for all adsorbents.

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