Leaching of Arsenic from Contaminated Soil Amended with Red Clay

Sumrit Mopoung[1*] and Prasak Thavornyutikarn[2]

[1]Department of Chemistry, Faculty of Science, Naresuan University,
Phitsanulok 65000 Thailand
[2]Department of Chemistry, Faculty of Science, Chiang Mai University,
Chiang Mai 50002 Thailand
[*]Corresponding author. E-mail: sumritm@nu.ac.th

ABSTRACT

The leaching of arsenic from contaminated soil amended with red clay was studied. The effects of water pH and amount of red clay amended in contaminated soil were investigated. It was shown that at the various pH values only small fractions of arsenic were leached as compared to the total amount present in the contaminated soil. The leaching of arsenic decreased with increased the amount of red clay from 0.5%, 1.0%, and 2.0% w/w in contaminated soil and decreased slightly with increased the pH of water form 3 to 5 and then increased sharply.

Keywords: adsorbent, arsenic, contaminated soil, leaching, red clay

INTRODUCTION

Arsenic is mobile within the environment and may circulate many times in various forms though the atmosphere, water, and soil before finally entering its ultimate sink (McBride, 1994). The arsenic movement in soils to ground waters is dependent not only on the total arsenic concentration of a site, but also on the soluble fraction of arsenic present. The immobility of arsenic in contaminated soils will in turn reduce the toxicity and pollution potential of arsenic-contaminated soils (Jain *et al*., 1999). Possible consequences of immobility of arsenic in a system containing mineral adsorbents are adsorption and precipitation (Elkhatib *et al*., 1984). Arsenic compounds tend to form insoluble complexes with soils and sediments (McBride, 1994). Arsenic can be immobilized through adsorption-coprecipitation with oxyhydroxide of iron and aluminum (Pierce and Moore, 1980; Edwards, 1994; Peng and Di, 1994; Wilkie and Hering, 1996; Fendrof *et al*., 1997). The movement of arsenic is significantly retarded due to adsorptive processes (Van Der Hoek and Comans, 1996; Corwin *et al*., 1999). Release of arsenic was related to the total iron and iron oxides (Clement and Faust, 1981; Moore *et al*., 1988; Mok and Wai, 1989). The pH has pronounced effect on the amounts of arsenate and arsenite adsorbed from a landfill leachate by clay minerals which results from the distribution of arsenic species present in the solution and in activation of the anion adsorption sites on the clay minerals.(Frost and Griffin, 1977; Goldberg and Glaubig, 1988). The Freundlich isotherm equation was successfully used to describe arsenate and arsenite adsorption over an initial concentration range of 25 to 200

mg/L arsenate for red clay (Mopoung and Thavornyutikarn, 2004). This may be attributed to the content and type of mineral of iron oxide and aluminium oxie in red clay which are Hematite or Kaolinite. Based on the Freundlich isotherm, it was concluded that the adsorption mechanism of arsenate or arsenite proceeds by means of an irrersible chemical reaction (Elkhatip *et al.*, 1984).

The objective of this work examined the ability of red clay (At km 30 Chaing Mai – Mae Sai Road, Doi Saket Distric, Chiang Mai Province, Thailand) for the reduction of mobility of arsenic by adsorption as a permanent compound with the specific amendments in contaminated soils. The contaminated soil was obtained from Ron Phibun District, Nakhon Si Thammarat Province, Thailand, and it is by-products of tin-mining activities. The Ron Phibun wasted soil is a highly complex, heterogeneous mixture of sulphide, silicates and oxide with high total concentrations of arsenic (Arrykul *et al.*, 1996).

MATERIALS AND METHODS

Red clay and contaminated soil were used in the investigation. Red clay was air-dried, then crushed and passed through the –80 mesh sieve. The contaminated soil is air-dried and passed through 2 mm sieve. A number of physical and chemical properties of red clay and contaminated soil 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 red clay. 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). Percent of water holding capacity (%WHC) of contaminated soil was determined by under standardized conditions (Raymond, 1990). 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).

The leaching experiment was modified from the method of Van Der Hoek and Comans (1996) and Esnaola and Millan (1998). Red clay was applied to the contaminated soil as a arsenic immobilizing additive on a 0.5%, 1.0%, and 2.0% w/w basis. Soil and additive mixtures, as well as the untreated soil were rehydrated to 70% of the water holding capacity (WHC) and equilibrated for 48 h. Then the wet soil mixtures were dried in oven at 105-110°C for 24 h. Porcelain crucibles with holes in the bottom were covered with filter paper and filled with 2.00 g of oven-dry soil mixtures. The crucibles was leached in triplicate for 24 h with 20 mL deionized water adjusted with 1 mol/L NaOH or 1 mol/L HCl (reagent grade, Merck) solution to eight different pH values (3.00-10.00±0.05). Flow through the soil mixtures were very slow (about 24 h). The leachates obtained were analyzed for total arsenic concentration by UV-VIS spectrophotometry (Johnson and Pilson, 1972).

All reagents for analyzing of arsenic are analytical reagent (Merck).

**Table 1** Chemical constituents and physical properties of red clay and contaminated soil.

| Constituents	Red Clay	Contaminated Soil
SiO_2 %w/w	32.9	55.37
Fe_2O_3 %w/w	24.8	10.10
P_2O_5 % w/w	0.12	0.11
Al_2O_3 %w/w	23.1	23.15
CaO %w/w	0.06	0.07
Na_2O %w/w	0.05	0.01
K_2O %w/w	0.12	0.15
MgO %w/w	0.33	0.01
MnO %w/w	0.12	0.0076
Total As mg/kg	1.1	839
pH 1:1	4.86	7.10
pH_{ZPC}	5.10	-
Surface area m^2/g	52.63	-
WHC % w/w	-	56.47
% cumulative retain of particle size		
< 45μm	70.30	10.77
45-850 μm	29.70	83.37
> 850 μm	0.00	5.86
Type of mineral	Hematite	Goethite
	Kaolinite	Kaolinite
	Quartz	Quartz

%w/w   = percentage of weight per weight

RESULTS AND DISCUSSION

Results of total arsenic leaching from contaminated soil and contaminated soil amended with red clay at various pH values are presented in Figure 1. It was shown that at the various pH values only small fractions of arsenic were leached as compared to the total amount present in the contaminated soil (839 mg/kg total As). The lack of leaching of arsenic suggests that arsenic is chemisorbed by adsorbent (Elkhatip *et al*., 1984). Due to the small amount of arsenic released. The leaching of arsenic decreased slightly with increased the pH form 3 to 5 and then increased sharply. This may be attributed to hydroxyl ions replacing arsenic on the sorption sites of adsorbent and arsenic is released into solution. Furthermore, the increasing negative adsorbent surface charge with increasing pH facilitates desorption of arsenic anions (Carbonell-Barrachina *et al*., 1999). This agrees with the report of Prasad (1994), that under oxidized alkaline conditions, soluble arsenic concentrations were high. It was observed that arsenic release decreased when the adsorbent was added to the contaminated soil. The magnitude of arsenic released was directly related to the amount of red clay in the contaminated soil. When red clay was added to contaminated soil to arsenic adsorption, arsenic can be adsorbed.

The arsenic released decreased with an increased in the amount of red clay from 0.5%, 1.0%, and 2.0% w/w. This may be attributed to the content of iron/aluminum oxide (Hematite and Kaolinite) and the particle size distribution of red clay (Table 1).
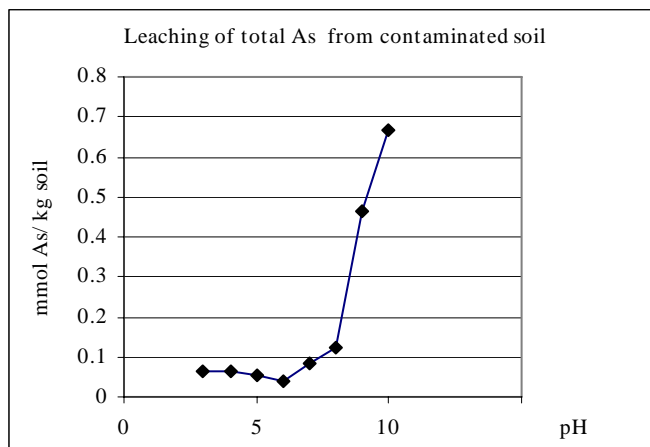
(a)
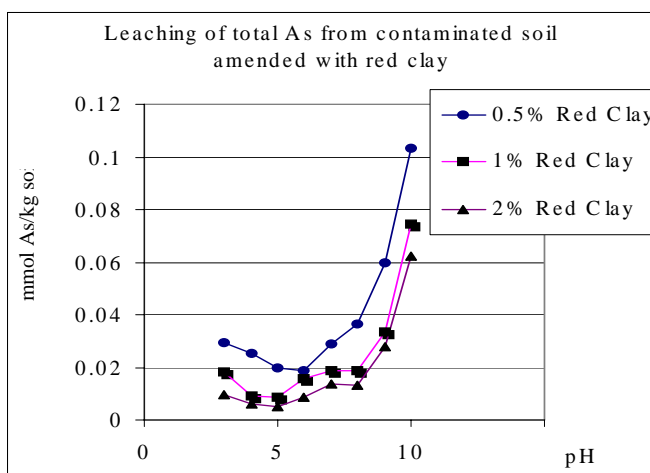
(b)

Figure 1   Leaching of total arsenic form contaminated soil (a) and contaminated
                  soil amended with red clay (b).

       The contaminated soil has a high content of large particles. But particle size of most of the red clay was fine. The effect of particle size, the adsorption of adsorbate increases as the diameter of the adsorbent particle decreases. This is due to the higher surface area available for adsorption in the small particles. Furthermore the diffusive path length into the interior of the adsorbent particles are reduced in the case of smaller particles, and the adsorbate species require less energy to jump from one active site to another, resulting in higher uptake by the adsorbent. Moreover,

small particles move faster in solution than larger ones, and hence sustain a greater shearing effect due to collisions and intraparticle effects on their surface (Prasad, 1994).

CONCLUSION

Red clay (Doi Saket Distric, Chiang Mai Province, Thailand) additions to contaminated soil (Ron Phibun District, Nakhon Si Thammarat Province, Thailand) and water pH have been shown to be important for arsenic leaching from contaminated soil. Decreased arsenic concentrations in leachates were paralleled by increased the amount of red clay from 0.5%, 1.0%, and 2.0% w/w in contaminated soil. Thus, the contaminated soil amended with red clay can be immobilized arsenic which would cause a decrease in the mobility of arsenic in the environment. Leaching of arsenic from contaminated soil depends on the pH values of the water. The leaching of arsenic decreased slightly with increased the pH form 3 to 5 and then increased sharply.

ACKNOWLEDGEMENTS

REFERENCES

Arrykul, S., Kooptarnon, K. and Wittayawarawat, W. (1996). Contamination of Arsenic, Cadmium, and Lead in Pakpanang River Basin, Nakhon Si Thammarat, Thailand. International Symposium on GEOLOGY AND ENVIRONMENT, Thailand, 309-318.

Black, C.A., Klute, A. and Page, A.L. (1986). *Methods of Soil Analysis* (2nd ed.) Madison,Wis. American Society of Agronomy, Wisconsin.

Carbonell-Barrachina, A., Jugsujinda, A., Delaune, R.D. and Patrick, W.H. (1999). The Influence of Redox Chemistry and pH on Chemically Active Forms of Arsenic in Sewage Sludge-Amended Soil. *Environ. Int.*, *25*, 613-618.

Clement, W.H. and Faust, S.D. (1981). The Release of Arsenic from Contaminated Sediments and Muds. Environ. *Sci. and health*, *16*, 87-122.

Corwin, D.L., David, A. and Goldberg, S. (1999). Mobilty of Arsenic in Soil from the Rocky Mountain Arsenal area. *Contaminant Hydrology*, *39*, 35-58.

Edwards, M. (1994). Chemistry of Arsenic Removal During Coagulation and Fe–Mn Oxidation. *J.AWWA*, *86*, 64–78.

Elkhatip, E.A., Bennett, O.L. and Wright, R.J. (1984). Arsenite Sorption and Desorption in Soils. *Soil. Sci. Soc. Am.J.*, *48*, 1025–1030.

Esnaola, M.V. and Millan, E. (1998). Effect of Acid Precipitation on the Mobilisation and Leaching of Heavy Metals from Contaminated Soils. *Environ. Tecnol.*, *19*, 567-578.

Fendrof, S., Eick, M.S., Grossl, P.R. and Sparks, D.L. (1997). Arsenate and Chromate Retention Mechanism on Goethite. 1. Surface Structure. *Environ. Sci. Technol.*, *31*, 315-320.

Frost, R.R. and Griffin, R.A. (1977). Effect of pH on Adsorption of Arsenic and Selenium for Landfill Leachate by Clay Minerals. *Soil. Sci. Soc. Am.J.*, *41*, 53–57.

Goldberg, S. and Glaubig, R.A. (1988). Anion Sorption on a Calcareous, Montmorillonitic Soil-Arsenic. *Soil Sci. Soc. Am. J., 52*, 1297-1300.

Jackson, M.L. (1965). *Soil Chemical Analysis*. Prentice-Hall, Englewood, 498.

Jain, A., Raven, K.P. and Loeppert, R.H. (1999). Arsenic and Arsenate Adsorption on Ferrihydrite: Surface Charge Reduction and Net OH⁻ Release Stoichiometry. *Environ. Sci. Technol.*, *33*, 179–1184.

Johnson, D.L. and Pilson, M.E.Q. (1972). Spectrophotometric Determination of Arsenic, Arsenate, and Phosphate in Natural Waters. *Anal. Chim. Acta.*, *58*, 289-298.

McBride, M.B. (1994). *Environmental Chemistry of Soils*. Oxford University, New York, 31-62.

Mok, W.M. and Wai, C.M. (1989). Distribution and Mobilization of Arsenic Species in the Creeks Around the Blackbird Mining District, Idaho. *Water Research*, *23*, 7-13.

Moore, J.N., Ficklin, W.H. and Johns, C. (1988). Partitioning of Arsenic and Metals in Reducing Sulfidic Sediments. *Environ. Sci. Technol.*, *22*, 432-437.

Mopoung, S. and Thavornyutikarn, P. (2004). Adsorption of Arsenate on Clays. *Naresuan University Science Journal*, *1*(1), 1-10.

Prasad, G. (1994). *Removal of Arsenic(V) From Aqueous System by Adsorption onto some Geological Materials*. John Wiley & Sons, 133-154

Peng, F.F. and Di, P. (1994). Removal of Arsenic from Aqueous Solution by Adsorbing Colloid Flotation. *Ind. Eng. Chem. Res*, *33*, 922–923.

Piece, M.L. and Moore, C.B. (1980). Adsorption of Arsenite on Amorphous Iron Hydroxide from Dilute Aqueous Solution. *Environ. Sci. Technol.*, *14*, 214-216.

Raymond, W.M. (1990). *Soils and Introduction to Soils and Plant Growth* (6th ed.) Prentice-Hall, Englewood Cliffs, New Jersey, 113-154.

Van Der Hoek, E.E. and Comans, R.N.J. (1996). Modeling Arsenic and Selenium Leaching from Acidic Fly Ash by Sorption on Iron (Hydr)oxide in the Fly Ash Matrix. *Environ. Sci. Technol.*, *30*, 517– 523.

Wilkie, J.A. and Hering, J.G. (1996). Adsorption of Arsenic onto Hydrous Ferric Oxide: Effects of Adsorbate/Adsorbent Ratios and Co-occurring solutes. *Colloids Surfaces A: Physicochem. Eng. Aspects.*, *107*, 97-110.