



Arsenate Adsorption Mechanism on Nano-ball Allophane by Langmuir Adsorption Equation

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crossref <http://dx.doi.org/10.5755/j01.erem.58.4.395>

(received in June, 2011, accepted in December, 2011)

Arsenic is considered as the synonym of death. High toxicity of arsenic in nature is a worldwide problem and often referred to as 20th -21st century calamity. High arsenic concentration has been reported recently from USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, Japan and India. Among all the countries Bangladesh and West Bengal of India are at the high risk. Thus arsenic disposal became an important task. In the present study an attempt is made to study the adsorption of toxic arsenic on allophanes.

The adsorption of arsenate on a low Si/Al ratio allophane (KyP) was found to be very effective in reducing the amount of arsenic below the toxic level. The examination of adsorption isotherm of arsenate on allophane by Langmuir theory indicated that arsenate adsorption increased with the increasing bulk solution concentration. The observed increase in the pH can be attributed to the ligand exchange on allophane. Aluminol groups, Al-OH or Al-OH₂, on allophane are responsible for the adsorption in soil.

Keywords: Allophane, Arsenic, Adsorption, Langmuir equation, mechanism.

1. Introduction

Arsenic (atomic number 33) is an omnipresent substance that rank 20th in the natural abundance comprising about 0.00005% of the earth crust, 14th in the sea water, and 12th in the human body (Mandal et al. 2002). The real cause of existence of arsenic still puzzles the scientists around the world. Arsenic is mobilized through the combination of various natural processes such as weathering reaction, biological activity and volcanic emissions, it also mobilize through the range of various anthropogenic activities. The environmental arsenic problems are because of its mobilization under natural condition. Leaching and soil erosion contribute to 2380×10^8 and 612×10^8 g/year of arsenic respectively, in dissolved and suspended forms in the ocean (Mackenzie 1979). However human activity such as mining, fossil fuel combustion, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create more harmful impact. The arsenic use has been deeply decreased in past decades but it is still used as wood preservatives.

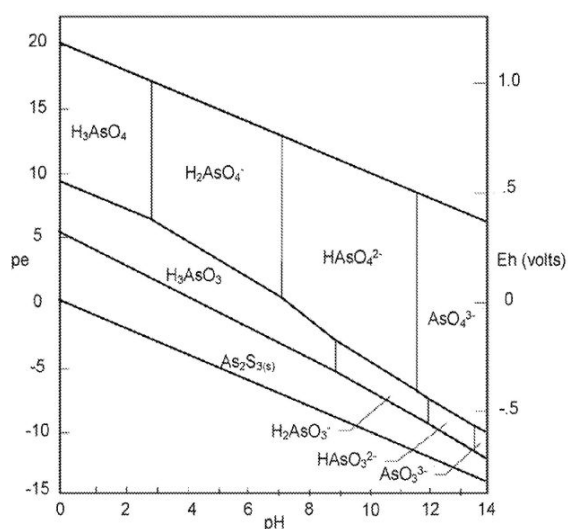


Fig. 1. Eh-pH diagram for aqueous arsenic species in the system As-O₂-H₂O at 25°C and 1 bar total pressure

Arsenic in nature. Arsenic abides in -3, 0, +3 and +5 oxidation states. Arsenious acid (H_3AsO_3), arsenic acid (H_3AsO_4), arsenates, methyl arsenic acid, dimethyl arsenic acid, and arsenic etc. are some of the environmental form of arsenic. Inorganic form of arsenic most often exist in water supplies (Bodek et al. 1998). The most common form of arsenic found in natural water is arsenious acid and arsenates ($H_2AsO_4^-$ and $HAsO_4^{2-}$) also called as arsenic (III) and arsenic (V).

Redox potential (Eh) and pH are the two important regulation factors of arsenic speciation (Fig. 1). (Brookins 1988 and Yan et al. 2000). Under the oxidizing condition $H_2AsO_4^-$ is dominant at low pH (less than about pH6) whereas under the higher pH $HAsO_4^{2-}$ became dominant. AsO_4^{3-} and H_3AsO_3 can be present at extremely high and low pHs, respectively. The dissociation of arsenious acid and arsenic acid is given in Fig. 2.

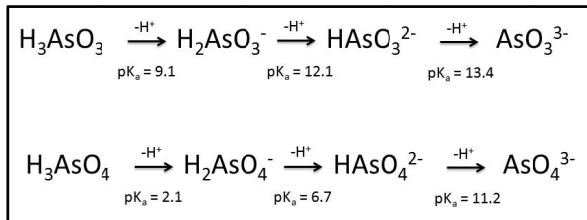


Fig.2. Dissociation of arsenious acid and arsenic acid. Allophane

Allophanes are the aluminum silicate with various compositions and are the main component of the volcanic ash and pumice (Wada et al. 1974). In 1976 Henmi and Wada for the first time reported the definite morphology of allophane. Henmi et al. (1976) separated allophane from the volcanic ash and weathered pumice grains and found a hollow spherical morphology. Nano-ball having diameter of 5nm and chemical composition from 0.5 to 1.0 with respect to Si/Al atomic ratio. Thus allophane is also referred as nano-ball allophane because of its size and hollow spherical morphology.

The ability of amorphous to adsorb heavy metals specifically has been reported by many authors (Forbes 1976; Abd-Elfattah 1981). However, they use whole soil or clay fraction (<2 μm) as sample. In the present study an attempt is being made to study the adsorption of toxic arsenic on nano-ball allophane.

2. Materials and methods

2.1. Allophane sample preparation

The allophane sample used in the present study was separated from weathered pumice grains. The pumice sample was collected from Kurayoshi, Tottori prefecture and hence called KyP. To eliminate the possible contamination of allophane sample with volcanic glasses, silica and imogolite proper care was taken while separating fine clay (<0.2 μm) from inner

part of pumice grain. The separation was proceeding by ultrasonification at 28 KHz and then dispersion at pH4 for low Si/Al ratio sample (Henmi and Wada 1976).

The dispersed sample was flocculated by NaCl solution, followed by washing with water to remove excess salts. Some amount of sample was freeze dried and then subjected to infra-red spectroscopy, thermal analysis and chemical analysis to ascertain the purity of the sample. The results confirmed that the sample is free from impurities. Atomic arrangements near the defect (pore) of hollow sphere nano-ball allophane are shown in Fig. 3.

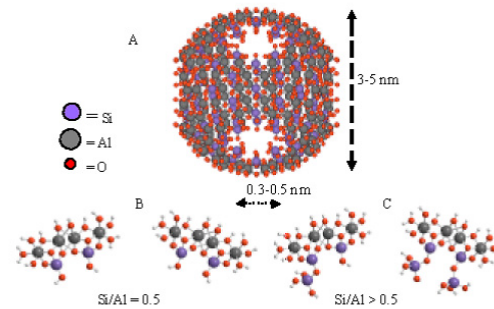


Fig.3. Chemical structure of nano-ball allophane (A) Full structure, (B) and (C) Atomic arrangement in cross section at pore region

2.2. Arsenate adsorption experiment

Arsenate adsorption experiment was conducted by treating 5 ml of suspension containing 50mg of allophane sample with 100 ml aqueous solution of di-sodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$) at different concentrations ranging from 0-100 μM. The initial pH was kept at 5 under 10mM NaCl as a background solution. The mixture was shaken for 24 hrs at room temperature and then centrifuged at 7500 rpm for 30 min. The clear supernatant was collected and is used further for measuring the equilibrium pH and concentrations of Si, Al and As using the polarized atomic absorption spectrophotometer (Hitachi Z-5000). The amount of arsenate adsorbed was calculated from the difference between initial and equilibrium arsenate concentrations, which was expressed in μmol/g.

The adsorption data were plotted according to Langmuir equation.

$$X = \frac{X_m K C}{1 + K C}$$

Where:

- X – the amount adsorbed per unit mass of allophane sample (μmol/g),
- K – the constant related to the binding energy (L/μmol),

C – the equilibrium concentration of adsorbate ($\mu\text{mol/L}$),
 X_m – the maximum adsorption ($\mu\text{mol/g}$).

The Langmuir equation is further expanded and discussed in later paragraphs.

3. Results and Discussion

3.1. Adsorption isotherm

The adsorption isotherm for arsenate on KyP sample was given in Fig. 4. The isotherm reveals that the adsorption of arsenate increases with the initial concentration of arsenate at pH 5. The increase is steep at lower equilibrium arsenate concentration, and then the curve gradually became plateau at higher equilibrium arsenate concentration. However, although not presented in the Fig. 4, further increase in equilibrium arsenate concentration above $20 \mu\text{M}$ caused irregular increase in the amount of arsenate adsorption. This may be attributed to the destruction or dissolution of allophane due to excess amount of arsenate in solution. This results in the formation of a new Al-OH or Al-OH₂ at the broken edge. Therefore, only the adsorption data until plateau region were used for further analysis

Al-OH and/or Al-OH₂ are responsible for the arsenate adsorption in soil and clay minerals (Parfitt 1979). Since KyP sample has higher content of Al (OH) (OH₂) group in the structure and because KyP has lower Si/Al ratio or greater Al atom contents per unit mass the adsorption of arsenate is higher. In the structure of allophane those groups are only located at the pores of the wall of hollow spherules (nano-ball) (Henmi and Huang 1985). It was reported earlier that the pH of equilibrium solution affects the amount of phosphate adsorbed on allophanic clays (Gunjigake and Wada 1981; Nanzjo 1988).

3.2. Langmuir adsorption equation

When the arsenate adsorption data in Fig. 4 was plotted according to Langmuir adsorption equation, two straight lines were obtained up to equilibrium concentration of $14.9 \mu\text{M}$ (Fig. 5). Two straight lines with a break at $0.5 \mu\text{M}$ of the equilibrium arsenate concentration were found. An assumption was made that there are two sites responsible for the arsenate adsorption (site I and site II) in allophane sample. Syres et al. (1973) also obtained two straight lines in their Langmuir plot for phosphate adsorption on soils, and they indicated the presence of two sites having widely differing affinity. Thus we rewrote the usual Langmuir equation as two terms Langmuir equation accordingly.

$$X = \frac{X_m^I K^I C}{1 + K^I C} + \frac{X_m^{II} K^{II} C}{1 + K^{II} C}$$

Where:

X – the amount of arsenate adsorbed,
 K – a constant related to binding energy,
 X_m – maximum adsorption of arsenate on allophane,
 C – the equilibrium arsenate concentration.

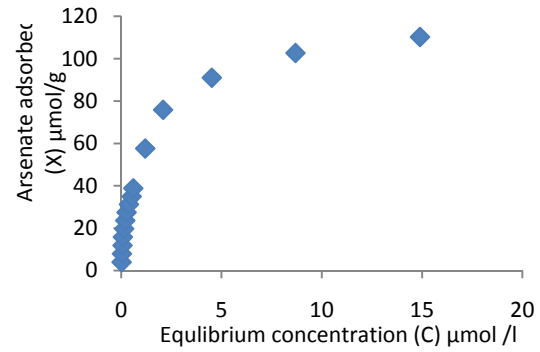


Fig.4. Adsorption isotherm of arsenate on nano-ball allophane

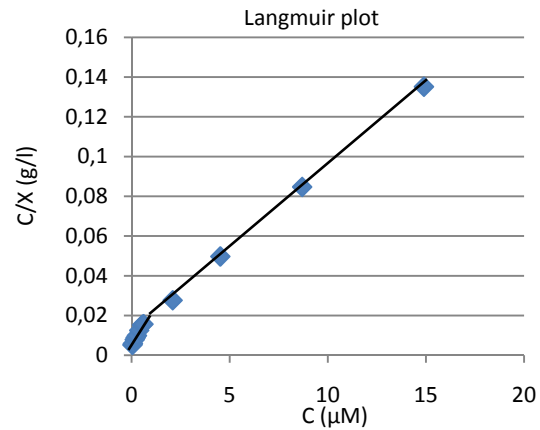


Fig.5. Langmuir plot for the adsorption of arsenate on nano-ball allophane. C; equilibrium concentration (μM), X; amount of adsorption ($\mu\text{mol/g}$)

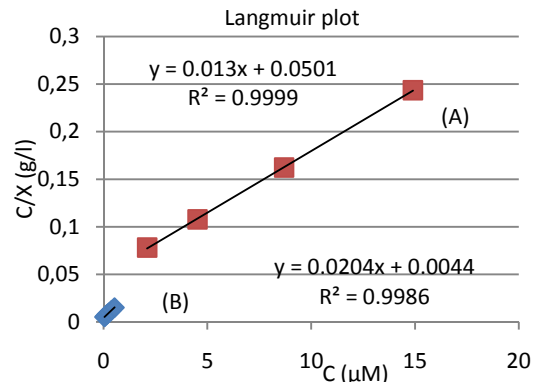


Fig.6. Langmuir plot for the adsorption of arsenate on nano-ball allophane after separation to sites I and II. (A) plot for site II after X^I was subtracted from each of the C values for the data points in site II and (B) isotherm for site I

The superscript I and II refers to the site I and site II respectively. The X_m^I and K^I values were calculated from the data at lower C values to the break point assuming it as site I for the arsenate adsorption. X^I was calculated for all C values. The X^{II} was calculated by subtracting X^I from X at each C values, then X_m^{II} and K^{II} was calculated. The data was re-

plotted with two sites I and II (Fig. 6) and the maximum adsorption and binding energy values were calculated according to the Fig. 6 : $X_m^I = 49.01 \mu\text{mol/g}$ and $K^I = 4.63 (\mu\text{M})^{-1}$ for site I whereas $X_m^{II} = 76.92 \mu\text{mol/g}$ and $K^{II} = 0.25 (\mu\text{M})^{-1}$ for site II (Table 1).

Table 1. Adsorption maxima (X_m) and binding energy constant (K) for two sites I and II each described by linear Langmuir plots

Adsorbent	Site I*		Site II [#]		X_m^{II}/X_m^I	K^I/K^{II}
	X_m^I	K^I	X_m^{II}	K^{II}		
	$\mu\text{mol/g}$	$(\mu\text{M})^{-1}$	$\mu\text{mol/g}$	$(\mu\text{M})^{-1}$		
Allophane (KyP)	49.01	4.63	76.92	0.25	1.56	18.52

*calculated from the data plotted in Fig. 5

[#]the value of X^I was subtracted from each of the X values for the data points in site II and the new regression equation was calculated for C/X^{II} against C for site II (see Fig.6)

4. Interpretation

The adsorption of arsenate on allophane was very similar with the adsorption of phosphate on nano-ball allophane and other soil having two adsorption sites (Johan 1997, Syers 1973). The present result obtained indicate that the isotherm consist of two linear relationship (site I and II) on plotting the data according to convectional Langmuir equation. The interesting finding of the data indicates that site II has relatively high arsenate adsorption capacity than site I but the binding energy of site I is significantly greater than site II (Table 1). The extensively different K values obtained for site I and site II of the Langmuir equation educates the possibility that distinct mechanism (probably involving different components) are involved in arsenate sorption. Allophane is known to form aggregates with many unit particles, creating outer and inner surface on and in the aggregates (Wada, 1989). It is conceivable that the aluminol groups, Al-OH and Al-OH₂ are responsible for the arsenate adsorption. Arsenate reacts with aluminol group inside the aggregate (site I) because this site has greater adsorption energy, then after saturating site I arsenate react with aluminol group at the outer surface of allophane (site II)

5. Conclusion

The sorption of arsenate was successfully represented by linear Langmuir isotherm with two sites (I and II). The inner surface of allophane aggregate may correspond to the site I while the outer surface on the aggregates may correspond to the site II for the arsenate sorption.

The environmental toxic level of arsenate is 0.6 μM , and from our experiment it was found that the initial arsenate concentration up to 10 μM was

decreased to below the toxic level. However higher arsenate concentration in the aqueous solution (more than 15 μM) causes partial dissolution of chemical structure of allophane. Hence allophane or composite material containing allophane can be a good adsorbent at the final stage of treatment of waters containing arsenate.

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