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Arsenic binding mechanisms on natural red earth: A potential substrate for pollution control

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Abstract

Natural red earth (hereafter NRE) was used as a novel adsorbent to examine its retention behaviour in different inorganic arsenic species (As (III) and As (V)) that are abundant in natural water. Adsorption isotherms were constructed at pH ~5.5 for As(III) and As(V) in 0.01 M $NaNO_3$ at 298K for 5 g/L NRE system. The initial arsenic [As(III) or As(V)] concentrations varied between $\sim 10^{-5}$ and $\sim 10^{-4}$ M. The experimental data were quantified using single site or stepwise Langmuir models. Sorption maximum, was observed at ~0.173 mM of As(V). To reach the maximum surface coverage of red earth at pH ~5.5 As(III) requires ~0.308 mM of initial loading. When compared to As (III), As(V) shows strong affinity for NRE surface sites. This study suggests the potential of NRE as a starting material in decontaminating water polluted with As species.

Keywords: Natural Red Earth; Arsenite; Arsenate; Arsenic removal; Surface complexation; Water treatment

1. Introduction

Arsenic, a carcinogenic substance, occurs in surface and subsurface waters through natural and anthropogenic activities. Recent studies have shown that the arsenic concentrations in drinking water are far surpassing the recommended guidelines of WHO and USEPA (10 μg/L) in tropical parts of the world such as Bangladesh, Thailand, West Bengal of India, Argentina, Chile, China, Hungary, Taiwan, Vietnam and many parts of the USA (Smedley and Kinniburgh, 2002). The arsenic crisis in Bangladesh and West Bengal of India is considered as the biggest outbreak of a mass poisoning in the history. It is estimated that nearly 60 to 75 million people inhabiting Bangladesh are at a potential risk of arsenic exposure, and several thousands have already been affected by chronic arsenicosis (Mukherjee and Bhattacharya, 2001). Therefore, there is a pressing need to develop a cost and technically effective arsenic removal technology. While the removal technologies have varying degrees of effectiveness in terms of arsenic removal, they depend mostly on commercially available materials such as alumina and other aluminium hydroxides, Iron coated sand, manganese oxides etc to minimise arsenic removal cost especially for the economically poorer parts of the world where the environmental health impacts are often the most severe.

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Arsenic can be removed from waters through coagulation/filtration, adsorption on activated alumina, separation by ion exchange resin, adsorption into hydrous ferric oxides, adsorption onto various iron oxides and adsorption/filtration by manganese greensand (Subramanian et al., 1997; Bajpai and Chaudhuri, 1999; Thirunavukkarasu and Viraraghavan, 2003) and by phytoremediation (Pickering et al., 2000). The United States Environmental Protection Agency (USEPA) has proposed ion exchange, activated alumina, reverse osmosis, modified coagulation/filtration and modified lime softening as Best Available Technologies (BAT) for arsenic removal.

Though, arsenic adsorption by activated alumina was studied by various researchers (eg: Thirunavukkarasu and Viraraghavan, 2003). They have shown that the rate of arsenite adsorption was much slower in compared to the arsenate adsorption. The highest arsenic removal using activated alumina was achieved at a pH close to 6 and arsenic removal decreased as the pH increases. However, oxidation of arsenite to arsenate is essential to make the ion exchange process effective (Thirunavukkarasu and Viraraghavan, 2003). It will be a separate process in the water treatment and the treatment efficiency was affected by the source water composition and the presence of sulfate drastically reduced the adsorption capacity. Although ion exchange is an efficient treatment system for arsenic removal from drinking water, its application is limited to small, medium scale and point-of-entry systems because of high treatment cost (USEPA, 1999).

Arsenic removal with iron oxides has been investigated recently. In a separate study, Thirunavukkarasu et al. (2003) performed arsenic removal with iron oxide coated sand, which was prepared through a high temperature coating process. Though most of these processes efficiently remove arsenic species from both natural-aqueous and human-induced environments they are cost intensive. Therefore there is an urgent need to develop a cheap, household level arsenic removal method for the well being of humans who are affected by arsenic toxicity.

Frequently, arsenic has showed its best correlation with iron in sediments (Bose and Sharma, 2002; Smedley and Kinniburgh, 2002). Therefore iron bearing minerals and iron containing oxides were used to study the arsenic removal by various researches (Manning and Goldberg, 1996; Fendorf et al., 1997; Thirunavukkarasu et al., 2003; Dixit and Hering, 2003; Genç-Fuhrman et al., 2004). The best arsenite adsorption was resulted in high pH values ($\text{pH} > 7$) while best arsenate adsorption was obtained in low pH values ($\text{pH} < 6$) (Manning and Goldberg, 1996; Goldberg, 2002; Genç-Fuhrman et al., 2004). Therefore to obtain a maximum adsorption these treatment methods need oxidation of arsenite to arsenate.

Vithanage et al. (2006) previously used natural red earth (NRE) to study the removal behaviour of arsenite and arsenate from water. However the variation of As adsorption as a function of different substrate loading or adsorbate loading were not examined in detail. Here, the As adsorption behaviour on NRE was studied at different initial adsorbate loadings to obtain the surface saturation level. The experimental results thus obtained were modelled assuming NRE as a variable charge surface. Plausible molecular structures of As — NRE complexes were simulated with semi-empirical molecular modelling method. Chemical method for As removal utilizing natural substrates as NRE will help in developing cost effective arsenic retention methodology.

2. Materials and methods

The material used in this study was obtained from the NRE deposit, overlying the limestone strata in the northwestern part of Sri Lanka. NRE is considered as an iron coated sand (Dahanayake and Jayawardana, 1979) and aluminium as well as iron is present as the active surface sites in this material (Vithanage et al., 2006). Mechanically sieved $<63\ \mu$ fraction of NRE was used for the experiments. The physiochemical parameters of NRE used for the study are the same used in the previous study (Vithanage et al., 2006). All the experiments were performed for 5 g/L concentration of substrate under 0.01 M ionic strength condition. SEM study was carried out to observe the surface characteristics of NRE without any chemical treatment.

2.1. Adsorption isotherms

Adsorption isotherms were measured at pH ~ 5.5 because arsenic adsorption on NRE recorded as high in between pH 4 and pH 7 (Vithanage et al., 2006). Therefore an average pH was used in this experiment. For each As(III) and As(V) in 0.01 M $NaNO_3$ at 298 K. The initial As(III) and As(V) concentrations were varied between $\sim 10^{-5}$ and $\sim 10^{-4}$ M. 0.106 M HNO_3 was used for pH adjustments. The solution ionic strength was 0.01 M $NaNO_3$. Prior to equilibration of 5 g/L red earth system for 24 h, gas N_2 was purged to the system to avoid CO_2 contamination. The 10 mL aliquots of red earth suspension were transformed to capped polypropylene tubes. Arsenic was spiked into the system, the tubes were equilibrated for 24 h at 100 rpm (EYELA B603 shaker) at 25 °C, and then pH was measured and recorded. After centrifugation, the supernatant was transferred by membrane filtration (0.45 μm) for arsenic analysis. Arsenic detection was carried out with flame method of the Atomic absorption spectrometer (GBC 933, Australia).

2.2. Data modelling

The arsenic adsorption were modelled with a single-site Langmuir adsorption isotherm,

$$\Gamma_{\mathrm{ads}} = \frac{k[M]\Gamma_{\max}}{(1+k[M])} \tag{1}$$

Where, Γ_{ads} is the amount of adsorbate adsorbed per unit area of surface (mol m^{-2}) and $[M]$ is the equilibrium solution concentration (mol m^{-3}) of adsorbate. The equation contains two adjustable parameters, $\Gamma_{\max}$, the maximum adsorption density and k, the equilibrium constant for the overall adsorption process. The Langmuir equation assumes that all adsorption sites have equal affinity for the adsorbate and that only monolayer adsorption occurs. Formula Eq. (2) was used to calculate Γ_{ads}.

$$\Gamma_{\mathrm{ads}} = \frac{[\mathrm{As}]_{\mathrm{ini}}[\mathrm{As}]_{\mathrm{fin}}}{[A][S]} \tag{2}$$

$[\mathrm{As}]_{\mathrm{ini}}$ and $[\mathrm{As}]_{\mathrm{fin}}$ are initial and final arsenic concentrations (mol m^{-3}), respectively; $[A]$ is surface area (m^2 g^{-1}) and $[S]$ is the solid content (g L^{-1}). The constants that were used for the modelling are given in Vithanage et al. (2006). The values of the adjustable parameters were estimated iteratively based on a non-linear least square fitting method.

3. Results and discussion

In the Scanning Electron Microprobe (SEM) photograph of the −63 μ fraction of NRE carried out under 800× magnification showed a surface coating of iron on euhedral grains.

3.1. Arsenic adsorption

The As(III) and As(V) adsorption density data were modelled using Langmuir model. Subsequently the bonding of As species on NRE were elucidated with the help of a molecular modelling method.

3.1.1. Arsenate adsorption

Solution species diagram for As(V), showed that at pH ~5.5 $H_2AsO_4^-$ is predominant with small amount of $HAsO_4^{-2}$. These species are negatively charged, adsorption will occur mostly on neutral or positive surface sites. Adsorption isotherms were constructed for both arsenic species based on the experimental results is shown in Fig. 1. The Adsorption isotherm which constructed for $[\mathrm{As(V)}]_{\mathrm{eqm}}$ vs. $[\mathrm{As(V)}]_{\mathrm{adsorption\ density}}$ is shown in Fig. 2a, and the lines represent the best fit obtained when modelled with one-site Langmuir equation.

However, the Freundlich adsorption isotherm (Fig. 2b), on log [As(V)]eqm vs. log $[\mathrm{As(V)}]_{\mathrm{adsorption\ density}}$ fit nearly linear in three different concentration ranges: 0.016–0.064, ~0.064–0.16 and ~0.16 mM of initial loading. The slope varies in the three different regions as less than 1, greater than 1 and ≈0. This implies adsorption does not correspond with a mono-layer model when the initial loading increases. At intermediate initial loadings there is the formation of multi-layers and at the higher concentrations, it reaches a saturated level.

This variation of adsorption density of As(V), does not intend the homogeneous surface sites. When pH ~5.5 NRE surface sites are tend to be positively charged as its $\mathrm{pH_{zpc}}=8.5$. Arsenate adsorption is governed by different reactive surface sites because of surface roughness. At the low initial concentrations, As (V) species tend to react with a most reactive surface site, $>\mathrm{FeOH_2^+}$. After the adsorption reaches to its maximum surface coverage, the next reactive site, $>\mathrm{AlOH_2^+}$, appear for adsorption. The Fig. 2b, shows total adsorption density increases in a higher slope. Finally, both sites reach their saturation limits indicating no considerable high rate of adsorption. When combining all these effects, generate a wide-range of adsorption energies that can subsequently result in a heterogeneous surface. However, a sorption maximum, which indicates a

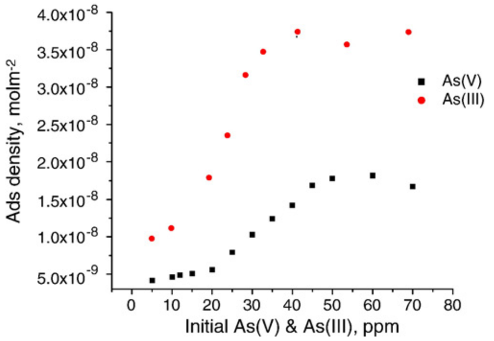

Fig. 1. Experimental results of adsorption isotherm of As(V) and As (III) constructed at pH=5.5. Circles represents As(III) and squares represents As(V). Background ionic strength of 0.01 M $NaNO_3$.

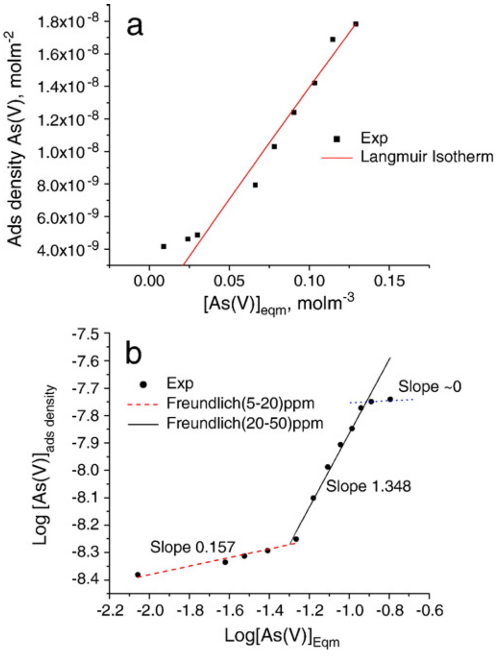

Fig. 2. a) Langmuir adsorption isotherm for As(V) on red earth at 0.01 M $NaNO_3$. pH = 5.5. Symbols represent experimental results and solid line represents calculated results using non-linear least square fit; b) Freundlich adsorption isotherm for As(V) species at 0.01 M $NaNO_3$. pH = 5.5. Symbols represent experimental results and solid and dotted lines represent calculated results using non-linear least square fit.

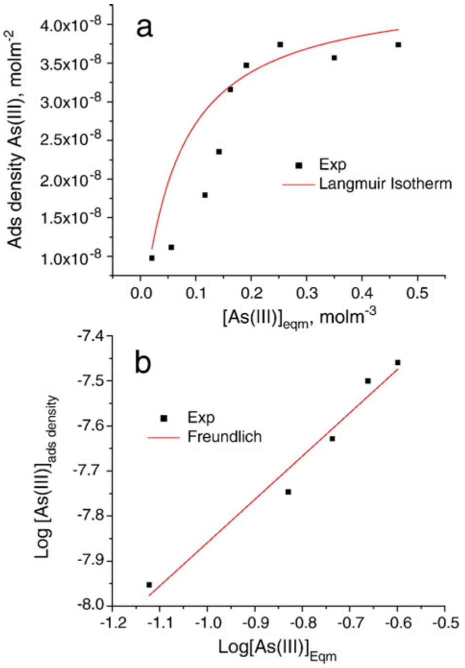

Fig. 3. a) Langmuir adsorption isotherm for As(III) on red earth at 0.01 M $NaNO_3$. pH = 5.5; b) Freundlich adsorption isotherm for As(III) species at 0.01 M $NaNO_3$. pH = 5.5. Symbols represent experimental results and solid line represents calculated results using non-linear least square fit.

saturation of sorption sites, was observed at ~0.173 mM of As(V) concentration. Therefore NRE can adsorb much more arsenate than most of the commonly used substrates for arsenic adsorption.

3.1.2. Arsenite adsorption isotherm

The values obtained for the solution species of As (III) at different pH values showed H_3AsO_3 is the predominant species at pH 5.5. The adsorption of As (III) onto red earth as a function of As(III) concentration in solution is shown in Fig. 3a. The adsorption of As(III) increases with increasing As(III) loading. The Adsorption maximum, which indicates a saturation of sorption sites, was observed at ~0.308 mM of As(III) concentration. In the case of AB (5 g/L) the results were fitted well with Langmuir isotherm with initial As(III) concentration range of 2 to 157 μM at pH ~7.0 (Genç-Fuhrman et al., 2004).

The As(III) adsorption isotherm (Fig. 3b), was nearly linear on a log–log scale, suggesting a monolayer formation of adsorption. This reveals that one site of NRE is enough to reach its saturated level. To reach the maximum surface coverage of red earth at pH ~5.5 As (III) requires ~0.308 mM of initial loading. Although, $\Gamma_{max\ As(III)}$ tends to be higher than that of As(V). The affinity of As(III) is higher than As(V) on NRE (c.f. Γ_{max}, and k values given in Table 1). However, in order to reach a saturation limit required initial loading of As (III) that is 0.3 mM higher than that of As(V).

3.2. Arsenic-NRE bonding mechanism

Both As(III) and As(V) species bond to the NRE surface. The nature of these complexes was calculated using an empirical molecular modelling method. In this

Table 1
Langmuir and Freundlich isotherm constants for As(III) and As(V) adsorption at pH 5.5

Isotherm	Arsenite	Arseante	
Langmuir			
Γmax/mol m^{-2}	4.483×10^{-7}	4.818×10^{-7}	
k/m^3 mol^{-1}	15.4275	0.2978	
R^2	0.981	0.939	
Freundlich		(5–20) ppm	(20–50) ppm
Γmax/mol m^{-2}	1.262234×10^{-7}	8.553×10^{-9}	3.039×10^{-7}
k/m^3 mol^{-1}	8.250×10^{6}	7.468×10^{8}	2.439×10^{6}
R^2	0.968	0.940	0.986

calculation no distinction was made between different surface sites (i.e. >AlOH and >FeOH). The overall aim was to calculate the As bond lengths and surface site density of most stable surface species. Calculated values for the As(V) bond lengths and surface site density was shorter and lower respectively than that of As(III). Both >AlOH and >FeOH sites were shown shorter bond lengths eg. 3.3 and 3.4 Å and 3.1 and 3.2 Å respectively for As(V) indicating strong bonding of As (V) to surface sites when compared to As (III) where the bond lengths were long when compared to As(V) in both >AlOH and >FeOH (3.5 and 3.8 Å) sites. The results of Fe–As distances were almost similar to the results of Fendorf et al. (1997) obtained for goethite–As surface structures. This indicates that >FeOH sites are selective in removing As species from aqueous solutions.

In the study of Genç-Fuhrman et al. (2004) where they have used 5 g/L Activated Bauxol (AB) at pH ~7.0 for their study with the initial arsenic concentration ranges from 2 to 152 μM there was no indication of multilayer formation in As(V) complexation. AB is consisting of Fe, Al and Si in its chemical composition and therefore show similarity to NRE but Al is not considered in their data modelling. Previous modelling results (Vithanage et al., 2006) showed that As(V) adsorption on >FeOH sites of NRE were high in the pH range of 4 to 7 and then >AlOH sites were used to adsorb As(V) than >Fe sites when pH>7. There will be different reactive surface sites because of surface roughness. This can be used as an evidence of a second reactive surface site of red earth. At the low initial concentrations, As(V) species tend to react with a most reactive surface site, $>FeOH_2^+$. After the adsorption reaches to its maximum surface coverage, the next reactive site, $>AlOH_2^+$, appear for adsorption.

4. Concluding remarks

Adsorption of As (V) on NRE is strong with a sorption maximum of ~0.173 mM of As(V) concentration and As(III) requires ~0.308 mM of initial loading for the saturation at pH 5.5. However, As (V) adsorption is deviated from the formation of monolayer assumption to multi-layer, when the initial loading increases. This is due to the complexation mechanism of two different reactive surface sites >FeOH and >AlOH. Therefore NRE can be used as a promising adsorption media for decontaminating water, which has polluted with inorganic As species. Further investigations are needed to investigate the adsorption behaviour of NRE in alkaline water or water with high anion concentrations such as phosphate.

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