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pH dependent Arsenic sorption in an Alfisol and an Entisol of West Bengal

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Abstract

Dependence of arsenic (As) sorption on pH was studied using two representative soils, one from alluvial soils (Entisol) and the other from lateritic soils (Alfisol) of West Bengal. For the lateritic soil, a decrease in As sorption was observed with increasing pH of the equilibrating solution at a lower concentration of As in the bathing solution. Interestingly, this trend got reversed at higher equilibrium As concentration. The alluvial soil also showed the above trend but such reversal occurred at a much lower concentration of As. These findings were related to the changing charge characteristics of the variable-charge surfaces with pH in the given soils and the solubility product principles governing the nature of the arsenic sorption products formed in the soils under study.

Additional Key words : Arsenic sorption, variable-charge surfaces, solubility product principle

Introduction

Arsenate (AsO_4^{3-}) and arsenite (AsO_3^{3-}) are the primary inorganic As forms in soils (Masscheleyn *et al.* 1991). Scientific evidence supports the view that arsenic is carcinogenic and that chronic arsenoses can result from low intake levels. Soil As can undergo oxidation-reduction and methylation-demethylation reactions in the soil (Brannon and Patrick 1987, Masscheleyn *et al.* 1991). Methylated arsenic oxyacids can be produced by a variety of microorganisms and their presence has been reported in a wide range of soils, sediments and waters (Masscheleyn *et al.* 1991). The total amount of As in soil and its chemical forms have an important influence on plant growth (Carbonell- Barrachina *et al.* 1997) and health of animal and human beings (Yan-Chu 1994).

Arsenic contamination in the groundwater reserves of West Bengal in 81 blocks, spread over 9 districts, has reached rather alarming proportion, affecting millions of people (Mandal *et al.* 1996; Sanyal and Nasar 2002). Consequently, knowledge of the interaction between soil constituents and arsenic has become imperative in view of the consideration that soil acts as the major sink for this toxin received by the soil-plant system through the use of contaminated groundwater as irrigation source. Moreover, it has been reported that the surface water bodies have remained effectively free of arsenic in the entire affected belt (Sanyal 1999). The present work was therefore carried out to identify the mode of interaction of As with the selected soils as affected by the nature of these soils.

Materials and methods

Surface soil (0- 0.15m) samples were collected from Goaltore (Alfisol) and Memari (Entisol) of West Bengal. The soil samples were air-dried and finely ground to pass through a 2-mm sieve before physical and chemical analysis by standard methods. The Goaltore soil is an Alfisol, acidic in reaction (pH 4.8) with 14% clay, 4 g kg $^{-1}$ organic carbon content, cation exchange capacity (CEC) 10 cmol (p+) kg $^{-1}$ and an electrical conductivity of 0.08 dSm $^{-1}$. The Memari soil is an Entisol, acidic in reaction (pH 5.9), with 16 % clay content, having the organic carbon content of 8 g kg^{-1}, CEC 19 cmol (p^{+}) kg^{-1} and electrical conductivity of 0.1 dSm $^{-1}$.

Air-dried and sieved soil samples (0.5 g) were equilibrated in centrifuge tubes at 35°C for 48 hrs with 50 ml of aqueous arsenic solution containing graded amounts (10 to 50 mg of $AsO_4{}^{3-}$ l^{-1}) of Na2HAsO$_4$. 7H$_2$O, adjusted to pH 4.5, 5.5, 6.5, 7.5, and 8.5, by adding appropriate amounts of 0.1*N* HCl or 0.1*N* NaOH. The tubes were shaken for 30 minutes twice a day and at the end of equilibration, samples were centrifuged and arsenate was determined in the supernatant liquid by the arsenomolybdate blue method (Portmann and Riley 1964). Simple linear regression between sorption data and pH of the supernatant were worked out, and the standard sorption parameters at pH 4.5, 5.5, 6.5, 7.5, and 8.5 were generated.

Results and discussion

For the Goaltore soil (Fig. 1, Table .), a decrease in As sorption with increasing pH of the equilibrating solution was observed. Being lateritic, the Goaltore soil contains large amount of pH– dependent charge in the clay fraction. With an increase in pH, the positive charge sites on variable-charge surface decreases causing a fall in As retention (Fig. 1). However, the above trend got reversed at higher range of As concentration, and an increase in As retention with pH was observed at 50 mg $AsO_4{}^{3-}$ l^{-1}. With increasing ionic strength, the activity coefficient of a particular ion is known to decrease in solution. To maintain the constancy of solubility products of the precipitated soil-arsenate compounds, including those sorbed on the soil surface, the As concentration in solution phase increases, and thus the desorption of sorbed As would be suppressed. At higher concentration of As, this effect would dominate over decline in As retention by increasingly negative soil colloidal surfaces at higher pH as mentioned above. This, aided by the ligand exchange at negative surface through a co-operative 1: 1 interaction of undissociated weak acid and the corresponding anion with the soil surface, may cause a monotonic increase of As sorption with soil solution pH.

Table 1. Specific arsenic adsorption ($mg.kg^{-1}$) by Goaltore and Memari soils at varying initial As concentrations and pH of equilibrium solution

pH	Initial As concentration ($mg\ AsO4^{3-}.l^{-1}$)				
	10	**20**	**30**	**40**	**50**
			Goaltore Soil		
4.5	0.29	0.29	0.91	0.82	0.59
5.5	0.19	0.20	0.73	0.80	0.77
6.5	0.10	0.11	0.55	0.77	0.95
7.5	0.006	0.02	0.37	0.75	1.13
8.5	-	-	0.19	0.73	1.31
			Memari Soil		
4.5	0.18	0.50	0.34	-	
5.5	0.14	0.41	0.31	0.14	
6.5	0.11	0.23	0.31	0.44	
7.5	0.07	0.06	0.30	0.71	
8.5	0.04	-	0.28	1.02	

Another complementary process that might work in unison to increase As sorption with pH at higher As concentration may be related to the buffering action of Na_2HAsO_4. The latter acts as a buffer because of partial hydrolysis of arsenate anion, which happens to be a strong (conjugate) base in water. Such hydrolysis generates free OH^{-1} ions *in situ*. The addition of 0.1*N* NaOH to raise the pH of the sorption medium tends to depress the above hydrolytic equilibrium causing higher concentration of arsenate capable of undergoing ligand exchange reactions. Such a process would be facilitated at a higher level of added As resulting in a concomitant increase of arsenate sorption with pH.

Obviously, both the above mentioned mechanisms would be more probable in a soil providing larger amounts of surfaces capable of sorbing As through ligand exchange, *e.g.*, the Goaltore soil, rather than the Memari soil (Figs. 1 and 2, Table 1). The latter soil essentially exhibits similar trends of variations of As sorption with pH as the Goaltore soil.

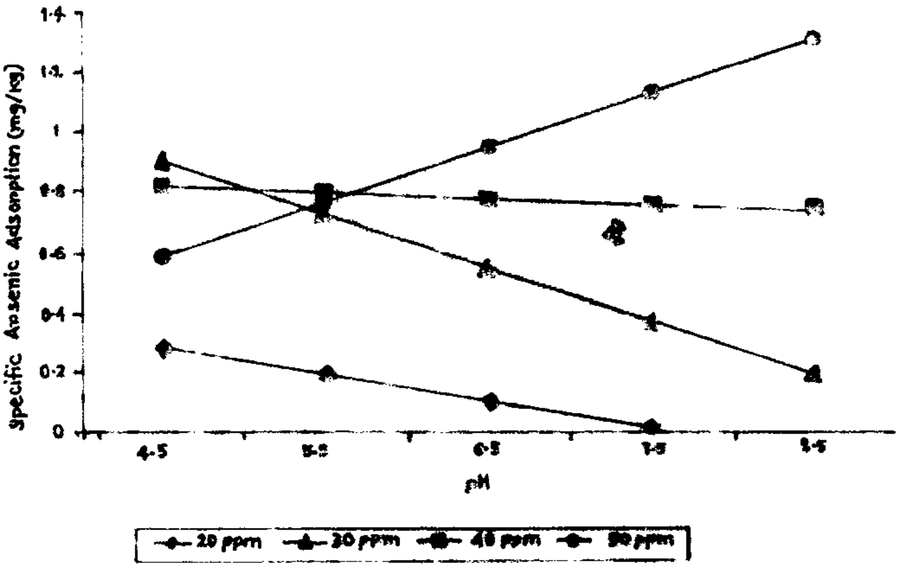

Fig. 1. Specific arsenic adsorption (mg kg^{-1}) by Goaltore soil at varying initial As concentrations and pH of equilibrium solution.

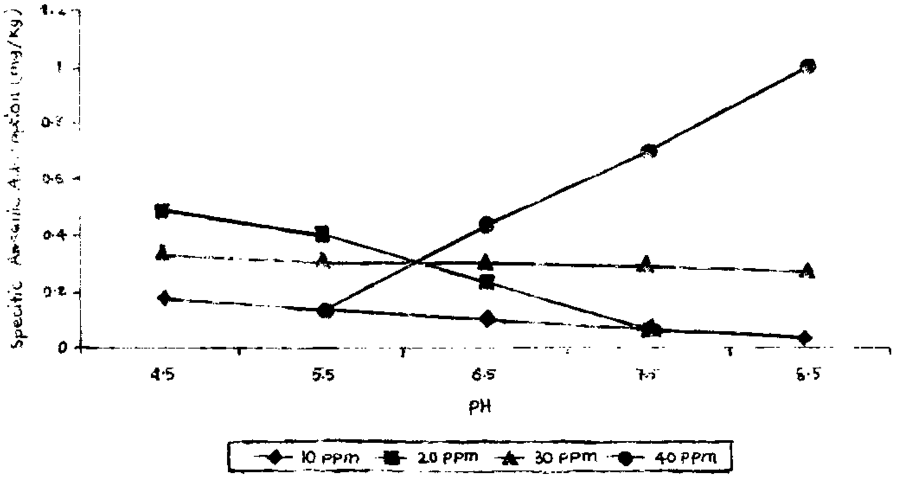

Fig. 2. Specific arsenic adsorption (mg kg^{-1}) by Memari soil at varying initial As concentrations and pH of equilibrium solution

However, the reversal of variation of As adsorption with pH, at higher concentration of the added arsenate (as observed in Goaltore soil and explained above), occurred at a lower level of As concentration in the Memari soil (Fig. 2) having comparatively lower amount of As sorbing components, such as the hydrous oxides of Al and Fe.

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