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Arsenic Sorption Characteristics of Four Agricultural Soils of Bangladesh

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Abstract: A study was conducted with four soils samples (0-15 cm) collected from different levels of arsenic (As) contaminated area where arsenic contaminated irrigation water from shallow tube well was used for rice cultivation to determine the maximum adsorption capacity, energy of adsorption and buffering capacity of As. Arsenic was determined by a Perkin-Elmer Analyst 100 atomic absorption spectrophotometer equipped with a FIAS-100 flow injection hydride generation system. The test soils showed a large capacity of arsenic adsorption. The application of arsenic progressively increased the equilibrium solution concentration of arsenic. At the lower levels of equilibrium concentration, the adsorption of arsenic linearly increased, but at greater levels of equilibrium solution concentration the rate of As adsorption decreased. Conventional adsorption equations-Langmuir, Freundlich and Temkin equations were used to describe arsenic sorption characteristics of soils. All soils were found to fit well in all the equations ($R^2 = 0.9052$ to 0.9974). Highest and lowest adsorption maxima were observed 2000 mg kg^{-1} in soil 2 and 3 and 1111 mg kg^{-1} in soil 4 respectively. The highest and lowest arsenic buffering capacity were observed 405 in soil 2 and 185 in soil 4 respectively. The highest energy of adsorption obtained for the soil 4, which showed lowest arsenic adsorption maxima and the lowest energy of adsorption obtained with soil 2 followed by soil 3, which showed the highest arsenic adsorption maxima. Arsenic buffering capacity was positively correlated with the maximum adsorption capacity of the soils ($r = 0.99$). The As adsorption parameters were highly correlated with clay content, FeO and MnO content of the soils and not with the total As content of the soils.

Key words: Arsenic, adsorption, soil

INTRODUCTION

Severe problems of ground water contamination by Arsenic have been reported from Bangladesh (Dhar *et al.*, 1997; Biswas *et al.*, 1998; Nickson *et al.*, 1998; Chowdhury *et al.*, 1999). In some areas of Bangladesh, ground water As concentrations reach 2 mg L^{-1} (Tondel *et al.*, 1999; BGS, 2000). The people of this region are not just drinking the contaminated ground water, but also using this water for crop irrigation. In Bangladesh, irrigation is mostly depended on ground water. Presently, 75% of the total cropped area and 83% of the total irrigated area are used for rice (*Oryza sativa*) cultivation (Dey *et al.*, 1996). Elevated As concentrations of up to 57 mg As /kg in soil collected from four district of Bangladesh are reported by Alam and Sattar, (2000). High As concentrations in soils and the use of irrigation water with high As may lead to elevated concentrations of As in cereals, vegetables and other agricultural products of As affected areas. After addition of arsenic contaminated irrigation water to soil most of the arsenic will be immobilized due to sorption onto (hydro) oxides of Al, Fe and Mn (McGeehan *et al.*, 1998), leaving a small

proportion in the solution. However, arsenic may accumulate in the soil solution to a considerable level once available sorption sites for arsenic on the soil particles have been occupied due to continued use of contaminated irrigation water. Soil properties such as texture (Frost and Griffin, 1977), nature of constituent minerals (Fordham and Norrish, 1983), pH (Smith *et al.*, 1999) and nature of other ions present in soils (Melamed *et al.*, 1995) are reported to have significant influence on the adsorption process in soil. Arsenic adsorption by soil may play an important role in reducing arsenic availability to plant and transfer the element to the food chain. The greater adsorption capacity and higher buffering capacity of soils could decrease the availability of arsenic to the plant and reduce movement of the element to the ground water and thus can be considered beneficial for the plant. Although, the arsenic pollution in the country is a great concern there is still a dearth of information on arsenic sorption behavior that are commonly found in the soils where irrigation is regularly conducted with As contaminated water. Considering the above-mentioned information a laboratory study was conducted with four soils from different levels of arsenic contaminated area to

determine the maximum As adsorption capacity, energy of As adsorption and As buffering capacity of these soils.

MATERIALS AND METHODS

Four agricultural soils (0-15 cm) from different levels of arsenic contaminated area, which received arsenic contaminated irrigation water for several years, were collected. The soils are designated as soil 1, soil 2, soil 3 and soil 4 for convenience (Table 1). The total As content of the soil 1, soil 2, soil 3 and soil 4 were 20.3, 26.3, 14.1 and 24.3 mg kg⁻¹ respectively. Collected soil samples were air-dried ground and passed through 2 mm sieve and stones, roots and plant debris were removed before the soils were air dried at 30 °C. The bulk sample was thoroughly mixed by hand and stored for analysis. The major physical and chemical properties of soil are presented in Table 1. To study the adsorption characteristics of the soils, one equilibration time was used: the adsorption isotherm was calculated after 48h of adding sorption solution. For equilibration, 20 ml solution of 0 to 250 µg As /ml as Na₂HAsO₄ · 7H₂O was added to 1 g of soils in 50 ml centrifuge tubes at room temperature (20° C). The soil solution was shaken for 48h by an end over end shaker. After equilibration the suspension was centrifuged at 10000 rpm for 10 minutes and the supernatant solution were filtered through Whatman No. 42 filter paper. The filtrates were analyzed for arsenic using a FI-HG-AAS using matrix-matched standards. Arsenic that had been lost from solution was considered to be sorbed. The arsenic adsorption data were interpreted from Langmuir, Freundlich and Temkin equations as described below:

Langmuir equation: The Langmuir equation can be expressed as:

$C/(x/m) = 1/kb + C/b$ (1): Where, C is the equilibrium As concentration (mg L⁻¹); x/m is the mg As sorbed per kg soil, b is the maximum adsorption capacity (adsorption maxima) and k is the constant related to binding strength. A plot of C/(x/m) versus C gives a straight line. The constant b and k were obtained from the slope and intercept.

Freundlich equation

$x/m = aC^b$ (2): By rearranging,

$\text{Log}(x/m) = \text{Log } a + b \text{ Log } C$ (3): Where, x/m is mg As adsorbed per kg soil, C is the equilibrium As concentration (mg L⁻¹) and a and b are constants. A linear plot of Log x/m versus Log C leads to a and b from the intercepts and slope respectively.

Temkin equation

$x/m = a + b \ln C$(4): Where, x/m is the amount of As adsorbed on unit mass of adsorbent (mg kg⁻¹), C is the equilibrium As concentration (mg L⁻¹) and a and b are constants. A plot of x/m against lnC gives a straight line. The constant a and b are obtained from intercept and slope. The b of the equation (4) is considered as the As buffering capacity.

Table 1: Selected properties of soils

Soils	pH	OC	Clay	FeO	MnO	P	Total As
		%		ppm			
Soil 1	7.05	0.89	22.2	1879	1156	16.98	20.3
Soil 2	7.33	1.00	28.9	1169	2103	27.71	26.3
Soil 3	7.63	1.12	30.5	1025	1457	21.63	14.1
Soil 4	7.22	1.62	18.5	2035	1023	35.40	24.3

RESULTS AND DISCUSSION

The application of chemical As increased solution As concentration in all the four tested soils. Quadratic equation in all soils described the relationship between added As and solution As (Fig. 1). The adsorption of As increased with the increase of As application. The

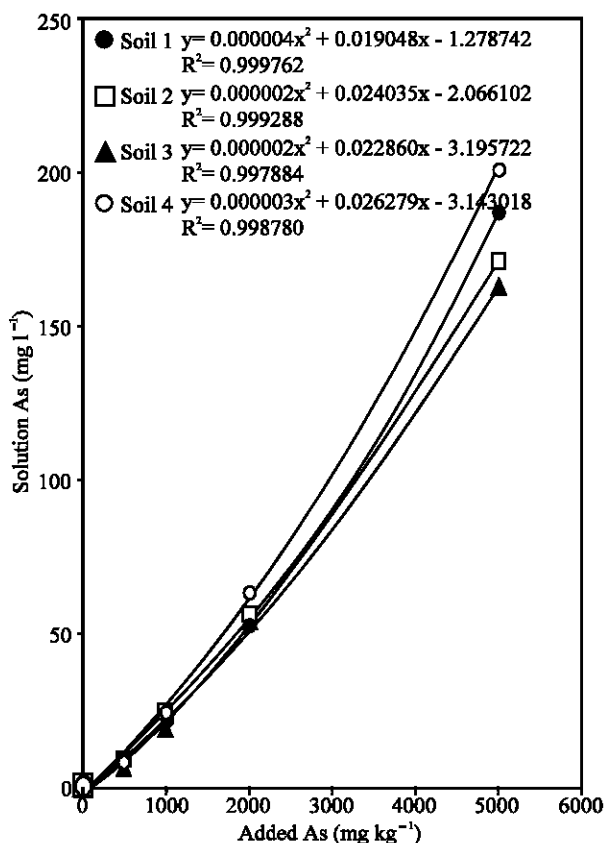


Fig. 1: Effect of As application on the solution As concentration in four soils studied

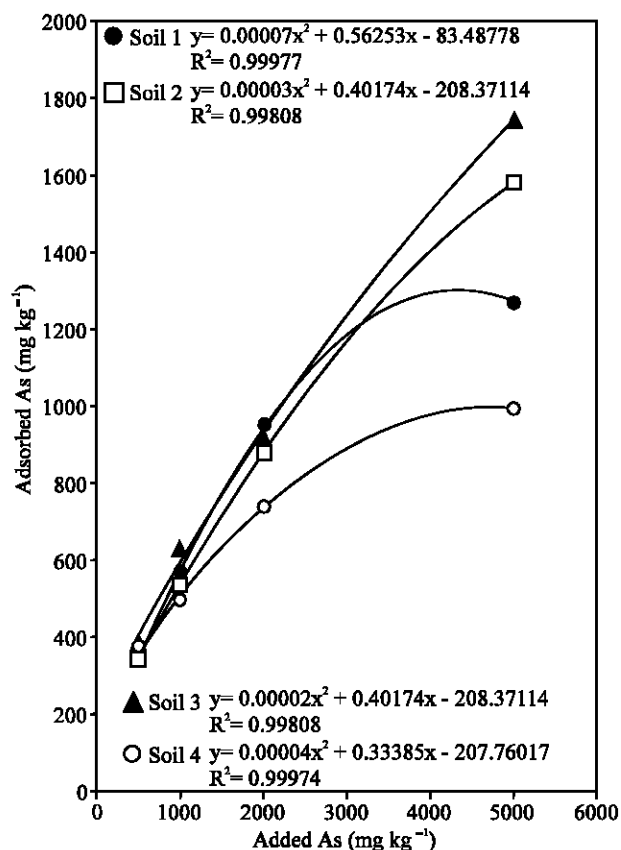


Fig. 2: Effect of As application on the As adsorption on four soils studied

increase of As adsorption with the increasing levels of As addition also followed quadratic equation (Fig. 2). The solution As concentration is usually smaller compared to adsorbed As in any soil, but there is a close relationship between these two As forms.

Soils maintain an equilibrium condition between solutions As and adsorbed As. The nature of the equilibrium between solution and adsorbed As largely determine the As supplying capacity of a soil. The relationships between equilibrium solution As and adsorbed As in four soils was same. The relationships were best explained by quadratic equation (Fig. 3). The relationships between equilibrium solution As and adsorbed As were also tested to fit the Langmuir, Freundlich and Temkin adsorption isotherm to calculate adsorption maxima, energy of adsorption and As buffering capacity of studied soil samples. The Langmuir adsorption isotherm explains the adsorption maxima and energy of adsorption. All three adsorption isotherms were found to fit well in all four soils (Table 2).

The arsenic adsorption maxima and energy of adsorption calculated from the Langmuir adsorption isotherm and

arsenic buffering capacity calculated from the Temkin adsorption isotherms are presented in Table 2. The highest arsenic adsorption maxima (b) was observed in soil 2 and soil 3 (2000 mg kg⁻¹ for both) and lowest arsenic adsorption maxima was found for soil 4 (1111 mg kg⁻¹) and for soil 1 it was 1429 mg kg⁻¹. The difference in b was attributed to the clay content, FeO oxide content and MnO content of soil (r = 0.99, -0.98 and 0.83 respectively) (Table 3). However, the soil 2 containing 28.9% clay had similar b with the soil 3, which had 30.5% clay. The pH and organic carbon showed a considerable influence and P and total As showed a little influence on the arsenic adsorption in the studied soils. Saleque *et al.* (2003) reported that b was partly attributed to the clay content of soil and the organic carbon, pH, Fe and Mn showed a little influence on the As adsorption. The energy of adsorption (k) for As calculated from the Langmuir adsorption isotherm showed that, the highest energy of adsorption was 0.042 g ml⁻¹ for soil 4 and the lowest 0.018 g ml⁻¹ for soil 2. Table 3 showed that there was a negative relationship between arsenic adsorption maxima and energy of adsorption.

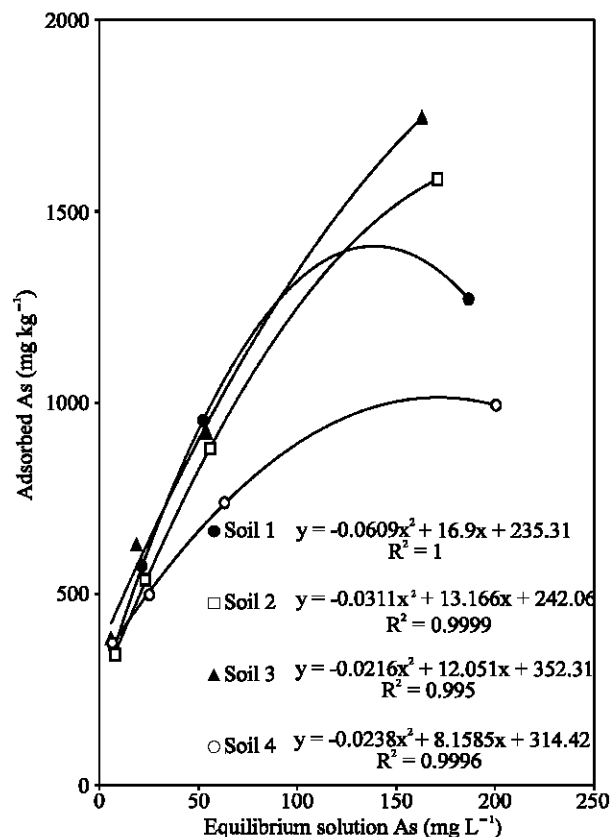


Fig. 3: Relationship between equilibrium As concentration and adsorbed As in four soils studied

Table 2: Arsenic adsorption fitness Langmuir, Freundlich and Temkin isotherms and sorption parameters

Soil	R ²			b ¹ (µg g ⁻¹)	k ² (µg ml ⁻¹)	BC ³
	Langmuir	Freundlich	Temkin			
Soil 1	0.9974	0.9687	0.9842	1429	0.037	294
Soil 2	0.9571	0.9968	0.9331	2000	0.018	405
Soil 3	0.9324	0.9902	0.9052	2000	0.024	395
Soil 4	0.9905	0.9840	0.9584	1111	0.042	185

¹ b = maximum adsorption capacity, calculated from Langmuir adsorption isotherm, ² k = energy of adsorption or adsorption affinity, calculated from Langmuir adsorption isotherm, ³ BC = buffering capacity of soil for arsenic, calculated from Temkin adsorption isotherm

Table 3: Correlation matrix of soil properties and arsenic adsorption parameters (n = 4)

	pH	OC	Clay	FeO	MnO	P	Tot As	b	k	BC
pH	1.00									
OC	0.05	1.00								
Clay	0.76	-0.56	1.00							
FeO	-0.83	0.44	-0.99	1.00						
MnO	0.37	-0.48	0.76	-0.77	1.00					
P	0.02	0.86	-0.39	0.26	-0.03	1.00				
Tot As	-0.56	0.22	-0.40	0.37	0.29	0.60	1.00			
b	0.70	-0.61	0.99	-0.98	0.83	-0.38	-0.30	1.00		
k	-0.62	0.54	-0.94	0.94	-0.94	0.21	0.07	-0.97	1.00	
BC	0.59	-0.72	0.97	-0.94	0.82	-0.50	-0.30	0.99	-0.95	1.00

Another apparent negative relationship between energy of adsorption and As buffering capacity of soil was observed. It was also observed that there was an apparent positive relationship (r = 0.99) between arsenic adsorption maxima and As buffering capacity of all studied soils. The similar results were reported by Saleque *et al.* (2003). The highest As buffering capacity of 405 was observed in soil 2 and lowest As buffering capacity of 185 was observed in soil 4. Therefore, the diffusion of As in soil 4 would be faster than that of other soils studied.

The study revealed that the test soils were different in arsenic adsorption capacity and arsenic buffering capacity. The soils showed higher As buffering capacity which indicate the ability of those soils to resist the change of soil solution As due to the application of As contaminated irrigation water.

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