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SORPTION KINETICS OF ARSENIC IN SOILS AS AFFECTED BY RESIDENCE TIME, SOLUTION CONCENTRATION AND CALCAREOUSNESS

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Abstract

A laboratory batch experiment was conducted using calcareous (Ishurdi series) and non-calcareous soils (Amjhupi and Dhamrai series) to evaluate the sorption kinetics of arsenic at three different imposed treatments. The rates of arsenic treatment were 5, 10 and 20 µg/ml. The sorption was observed at 2, 4, 6, 8 and 24 hour residence time. Arsenic sorption increased with increasing residence time from 2 to 24 hour irrespective of the calcareousness of the soil. An amount of 85.22 µg/g As was found to have been sorbed by the calcareous soil (Ishurdi series) after 24 hour of residence time while in a non-calcareous soil (e.g., Dhamrai soil) the amount sorbed for the same residence time was 57.75 µg/g at 20 µg/ml As solution concentration. The highest solution concentration of arsenic (20 µg/ml) caused the highest sorption. The most significant sorption with time has occurred for the Ishurdi soil (R^2 = 0.9610**) followed by the Amjhupi (R^2 = 0.9464**); and Dhamrai soils (R^2 = 0.9350**). In most of the cases the Langmuir model best described the sorption of As. This paper attempts at predicting the sorption mechanism of arsenic in soil environment which might be helpful in devising a comprehensive model for arsenic retention and mobility as well as the As toxicity and thereby ascertain its chemistry in soil.

Introduction

Contamination of ground water by arsenic in the deltaic region, particularly in the Gangetic alluvium of Bangladesh has become one of the world's most important natural calamities.(1) Land and agricultural sustainability in Bangladesh is being threatened due to the use of arsenic contaminated water.(2) High levels of arsenic have been detected in 61 out of 64 administrative districts, the southern, south-western and north-eastern regions of the country are worst affected.(3) Since arsenic in groundwater was recognized as a potential threat to human life, much effort has been directed towards ensuring safe drinking water either through mitigation techniques or through finding alternative water sources. Even when alternative sources of water are used for drinking purposes, irrigating soils with As contaminated water however, raises the concentration of its buildup in soil and

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subsequent entry into the cultivated crops.[4] A few studies have revealed that the average background concentration of As in Bangladesh is much below 10 mg/kg soil.[3,4] However, in some areas the concentration has been found to be more than 80 mg/kg soil.[5] The soil As varies both spatially and vertically. The soil formation and the aquifer characters control the spatial variation, while the vertical distribution is controlled by the clay contents.[6] The load of As in soil has been calculated to be as high as 5.5 kg/ha/yr through irrigation for certain crops.[7] Irrigating soils with As contaminated water raises the concentration of its buildup in soil and subsequent entry into the cultivated crops.[8] Irrespective of the source or chemical species of As contaminating the soil, its mobility, bioavailability and long term fate will depend to a large extent on its reactivity with the soil solid phase particularly by sorption-desorption mechanisms. Whether As enters the soil in a readily soluble form or is gradually solubilized from more complex As-containing materials, it is likely to be sorbed from solution on to the surfaces of soil constituents. The mobility of As in soil decreases with time, a process sometimes referred to as natural attenuation. For example, the effect of time on the distribution of As between different soil fractions following the addition of sodium arsenate to the soil were examined and found that over a period of 36 weeks there was a substantial decrease in the water solubility of the applied As.[9] Leaching of As from soil has also been shown to be affected by time and was found that increasing the period of contact clearly decreased the subsequent leaching of As, particularly during the period between 18 hours and 15 days.[10] Though much research has examined the sorption of As species in soils[2,11] no work has yet been focused on sorption kinetics of As in Bangladesh soils. Bangladesh is located in the floodplains downstream of the rivers Ganges-Brahmaputra covering the calcareous and non-calcareous soils and there are some direct and indirect references of occurrence of As in the upstream of the rivers carrying water and sediments.[12] The mobility as well as the sorption-desorption of As over time thus demand thorough research. This work studies the kinetics of As sorption in soil over time that is likely to provide a better understanding of its long term retention in soil or its leaching back into the subsurface so that proper management strategy could be taken to abate arsenic toxicity in the food chain.

Materials and Methods

Three soils were selected for the study. Two of the soils represented the Gangetic alluvium- one calcareous and the other one non-calcareous, while the third soil, also a non-calcareous, represented the Brahmaputra alluvium. The three soils represented the Amjhupi, Ishurdi and Dhamrai series, respectively. The descriptions of the three series are given in Table 1.

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The soil samples were collected and prepared and the common physical, chemical and physicochemical properties of the three soil series were analyzed following the standard methods.[13]

Table 1. Location and correlation of general soil types of the three soil series with the US Soil Taxonomy.

Soil series	Location	Geo-reference	General soil type	USDA* soil taxonomy
Ishurdi	Noapara, Jessore Sadar	89°13.235′ E & 23°11.118′ N	Calcareous dark grey floodplain soil	Aeric Andoaquepts
Amjhupi	Shatakhali, Shalikha	89°19.764′ E & 23°20.247′ N	Non-calcareous dark grey floodplain soil	Aeric Andoaquepts
Dhamrai	Sombhag, Dhamrai	90°11.250′ E & 23°54.116′ N	Non-calcareous grey floodplain soil	Typic Andoaquepts

(Source: USDA = United States Department of Agriculture[23], * Soil Survey Staff.[24])

Equilibration procedure: The sorption studies were carried out in batch mode where a series of 50 ml polythene/plastic centrifuge tubes were used. In each tube 5 g soil sample was weighed. Twenty five ml each of the As solution, (which was made from $NaAsO_2$) were added to the tubes. There were three treatment rates for arsenic solution- 5, 10 and 20 µg/ml along with the control (0 µg/ml). All treatments were replicated three times. The tubes were shaken on a reciprocating shaker (50 turns/min) for two hours and were allowed to equilibrate at a constant temperature (room temperature) for 2, 4, 6, 8 and 24 hours, respectively. It was established from a preliminary study that two hour shaking followed by 24 hours rest was sufficient for the system to equilibrate. Immediately following the equilibration period, the suspensions were centrifuged at 2000 rpm (2000 g) over 5 - 50 minutes and filtered and the residues were collected.[14,15] Arsenic concentrations in the supernatant were determined with a Varian Spectraa-220 Atomic Absorption Spectrophotometer and used for sorption calculation. All assays were carried out in triplicate and only the mean values are presented in the text. Adsorption of As by the soils (X) was calculated by deducting the value in the equilibrium solution (C, supernatant) from the value of the original solution (C_0). The zero As treatment was used as background As for the experiment and these values were subtracted from the others to correct for the As that was released from the untreated soil. The following formula was used for the calculation.[15]

$$x = \frac{V_0C_0 - V_1C_1}{W}$$

where,

X = amounts of As adsorbed (µg/g soil),

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V_0 = initial volume of As solution (ml),

C_0 = initial concentration of As solution (µg/ml),

V_1 = total volume of equilibrating solution (ml),

C_1 = final concentration of As in equilibrating solution (µg/ml),

W = weight of soil taken (g).

The following form of the Langmuir adsorption equation[16] was tested to calculate the adsorption coefficients:

$$\frac{C}{X} = \frac{1}{kb} + \frac{c}{b}$$

Where,

C = equilibrium concentration of As in solution (µg/ml),

X = amounts of As adsorbed (µg/g),

b = adsorption maximum (µg/g),

k = constant related to the bonding energy of the soil (µg/g).

A plot of C/X versus C was made for each of the three soils. The values of adsorption maximum (b) and bonding energy (k) were calculated from slope ($1/b$) and intercept ($1/kb$) of the plot, respectively. All data were subjected to statistical analysis by MINITAB package; regression analyses were performed and the values of regression coefficients are discussed in the text.

Results and Discussion

The common physical, chemical and physicochemical properties of the three soil series were analyzed and the results of the analyses are presented in the Tables 2 and 3. The sorption pattern of the soils for 5, 10 and 20 µg/ml As treatment over time are presented in Figs. 1, 2 and 3. The sorption of arsenic for the three soils as affected by increasing concentration of arsenic along with increasing residence time are represented in Fig. 4. The regression analyses between the sorption capacities by the soils with time were performed. The experimental proofs of the data are calculated from the 'Langmuir Adsorption equation' from which the Langmuir coefficients i.e., bonding energy (k) and adsorption maximum (b) are calculated. The values of the coefficients 'k' and 'b' are presented in Table 4. The statistical significance of the correlation coefficient 'r' for C/X versus C (from Langmuir adsorption equation) is also presented in Table 4.

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Sorption of arsenic has been found to differ significantly from one soil to another, with respect to 'Residence time', 'Concentration of arsenic in solution' and 'Variation in the calcareousness of the soils'.

Table 2. Moisture content, particle size distribution and textural class of the soils studied.

Soil series	Moisture content (%)	Sand (%)	Silt (%)	Clay (%)	Textural class
Amjhupi	5.6	37.4	34.5	28.1	Clay loam
Ishurdi	9	35.1	33	31.9	Clay loam
Dhamrai	1.6	34.9	61.1	4.7	Silt loam

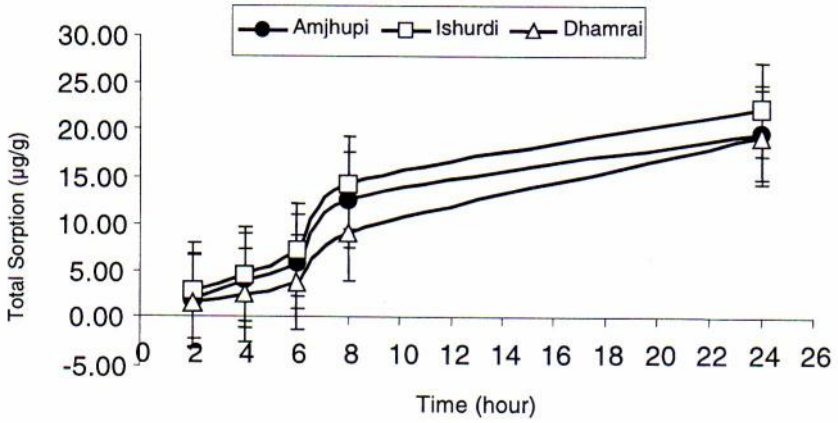

Fig. 1. Sorption of As by the three soils with increasing residence time at 5 µg/ml As treatment.

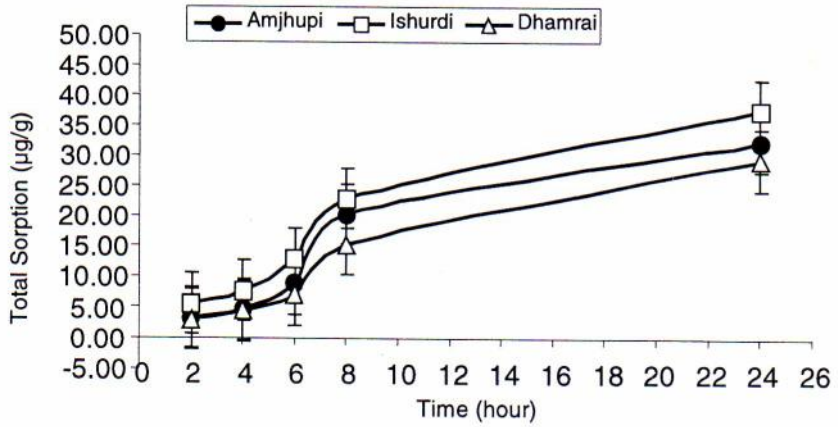

Fig. 2. Sorption of As by the three soils with increasing residence time at 10 µg/ml As treatment.

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Effect of residence time: As sorption increased with increasing residence time in all the three soils (Figs. 1, 2 and 3). There was a sharp increase in As sorption from 2 to 8 hour of residence time while after 24 hour, sorption in all soils were higher than the initial sorption. However, Ishurdi soil showed a relatively higher sorption than either Amjhupi or Dhamrai soil. The maximum sorption (85.22 µg/g) was observed for the calcareous soil i.e. Ishurdi soil followed by the non-calcareous soils Amjhupi (72.84 µg/g) and Dhamrai (57.75 µg/g) at 24 hour of sorption period. The lowest value of sorption was observed for the Dhamrai soil (1.63 µg/g) at 2 hour sorption. The regression analysis showed that the most significant sorption with time

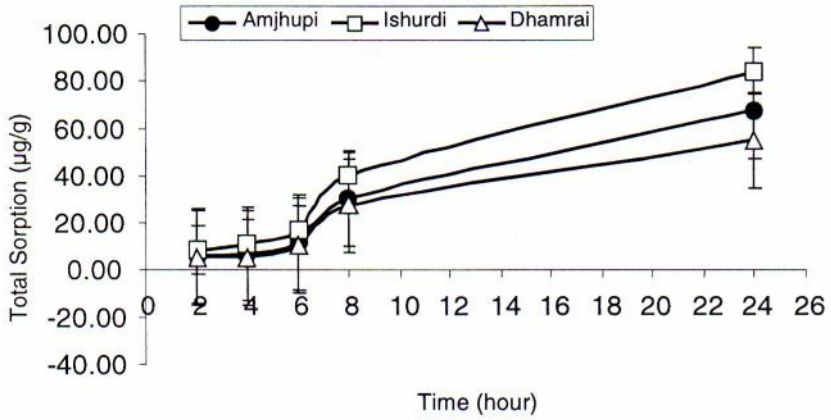

Fig. 3. Sorption of As by the three soils with increasing residence time at 20 µg/ml As treatment.

has occurred for the Ishurdi soil (R^2 = 0.9610**) followed by the Amjhupi (R^2 = 0.9464**); and Dhamrai soils (R^2 = 0.9350**), the latter two being non-calcareous. This indicates that, the sorption of As increases with increasing residence time and the calcareous soil have a relatively higher sorption capacity than the non- calcareous one. Or, alternatively, it could be postulated that calcareous soils hold As more tenaciously than the non-calcareous ones. This result is supported by the results of O' Reilly and others[17] where it was found that arsenic sorption on goethite increased with time. Sorption was initially rapid, with over 93% arsenate being sorbed in a 24-hour-period at pH 6.0. Similar sorption behavior was observed at pH 4.0. Yet, in another study, adsorption of As has been shown to be rapid initially and decreased with increasing equilibrium time.[11]

Effect of solute concentration: The rate of sorption increased with increasing concentration of As in the solution. At the highest concentration of arsenic i.e. at 20 µg/ml, the sorption of arsenic was the maximum for all the soils (Fig. 4) with values

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of 85.22, 72.84 and 57.75 µg/g for Ishurdi, Amjhupi and Dhamrai soils, respectively. In this case the sorption of arsenic followed the trend: Ishurdi > Amjhupi > Dhamrai.

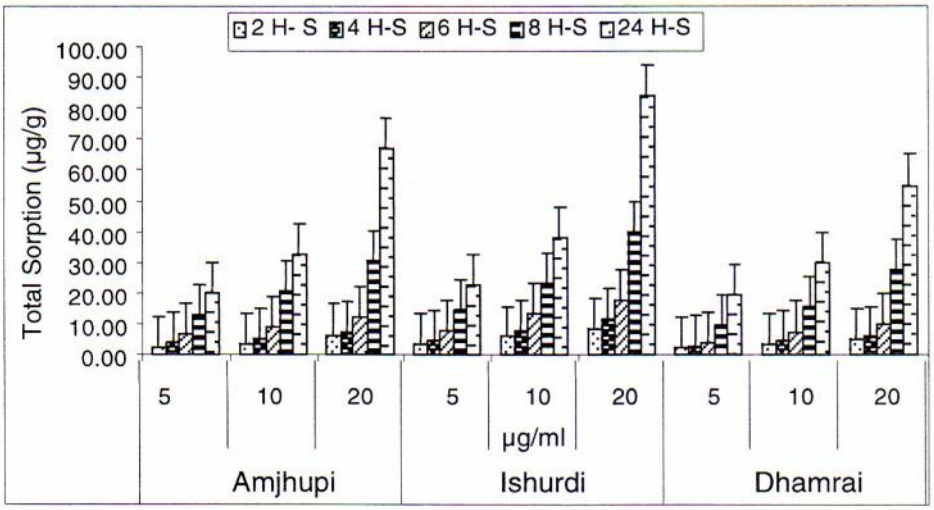

Fig. 4. Sorption of As for the three soils as affected by increasing concentration of As along with increasing residence time (2 H-S = sorption after 2 hours; 4 H-S = sorption after 4 hours; 6 H-S = sorption after 6 hours, 8 H-S = sorption after 8 hours and 24 H-S = sorption after 24 hours).

It is thus obvious that the quantity of As present in solution will have a positive effect on its sorption by soil. The magnitude of this sorption however, will depend on the calcareousness of the soil. Previous[15] study showed that highest sorption of arsenic (193 µg/g soil) was observed when the initial concentrations of As in solution was increased from 0 to 10 µg/ml. Typically, As sorption by soil increases with increasing additions of As to the soil, sorption increasing steeply at low solution As concentrations and tending to plateau at higher concentration.[18] The observed results for the calcareous and non-calcareous soils in the present study followed this pattern.

Variation in the soil properties: In the present case, for all the soils, sorption of arsenic was at its maximum for the calcareous soil (Ishurdi). The magnitude of As sorption varies greatly among different soils perhaps due to variations in soil characteristics.[18-20] It needs to be mentioned here that the Ishurdi soil contains free carbonate (9.3%) which was absent for the non-calcareous soils, and this free carbonate might have an effect on the sorption-desorption of arsenic. Arsenic sorption varies from soil to soil depending on certain soil properties like pH, redox potential, clay mineralogy, organic matter content etc.[21] The organic matter content of the Ishurdi series (1.1%) is higher than the other two non-calcareous soils. Moreover, from the textural analysis, it was found that the clay content of Ishurdi soil (31.9%)

Table 3. Various chemical and physicochemical properties of the soils (Amjhupi, Ishurdi, Dhamrai).

Soil series	pH	Organic carbon (%)	Organic matter (%)	Total N (%)	Total As	EDT A As	Water soluble As	Free CO_3^{-2}%	CEC meq (%)	Exchangeable cations meq (%)			
										Ca	Mg	Na	K
Amjhupi	6.89	0.47	0.81	1.08	4.2	0.64	0.01	N.D.	35.4	22.5	7	0.6	0.4
Ishurdi	7.73	0.62	1.1	0.57	5.75	0.85	0.03	9.3	41.6	31.3	4.5	0.5	0.4
Dhamrai	7.08	0.22	0.38	0.3	3.62	0.32	N.D.	N.D.	15.4	8.3	2.5	0.2	0.2

N.D. = Not detected.

Table 4. Langmuir coefficients- adsorption maxima, b (µg/g); bonding energy, k (µg/g) and Correlation coefficient between C/X and C (C is the equilibrium concentration of As in solution, µg/ml; X is the amounts of As adsorbed, µg/g), for the three soil series.

Time (h)	2			4			6			8			24		
Soilseries	b	k	r	b	k	r	b	k	r	b	k	r	b	k	r
Amjhupi	19.45	0.02	0.96	9.02	0.16	0.98	15.73	0.16	0.99	44.77	0.15	0.99	82.83	0.33	0.44
Ishurdi	20.47	0.04	0.97	19.28	0.08	0.99	18.14	0.32	0.94	67.35	0.11	0.96	92.79	0.52	0.59
Dhamrai	16.99	0.02	0.99	8.21	0.10	0.98	19.61	0.06	0.95	61.84	0.05	0.86	76.47	0.22	0.89

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is higher than either the Amjhupi (28.1%) or the Dhamrai (4.07%) soil. The organic fraction has a significant influence on adsorption[21] and the mechanisms involved in the retention by organic matter appear to include complexation and adsorption as well as ion exchange.[22]

From Table 4 it can be seen that the Langmuir model best describes the adsorption of As with increasing residence time. Considering the b parameter (adsorption maximum) of the Langmuir equation, it is observed that the maximum sorption after 24 hours was obtained for Ishurdi soil (92.79 µg/g), followed by Amjhupi (82.83 µg/g) and finally for Dhamrai soil (76.47 µg/g). The bonding energies for As represented by k (Table 4) were higher for the soils having the highest adsorption maxima (b), all of which indicate the influence of different soil properties.

The research showed that at longer residence time and at higher solution concentration the sorption of arsenic increased. Soil properties, especially the calcareousness of the soil might have a bearing on both the sorption-desorption mechanisms of arsenic. The phytoavailability of arsenic in soils could be related to the desorptivity of soils. Further research on desorptivities of soils and the availability-uptake relationship of As by plants is emphasised.

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