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ADSORPTION ISOTHERM OF ARSENIC BY SELECTED SOILS OF BANGLADESH

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Abstract

An investigation was conducted to study the adsorption isotherm of arsenic in various soils from Bangladesh, characterized by a wide range of physicochemical properties. Arsenic solutions at concentrations of 0, 25, 50, 100, 200, 500, 1000, and 2000 µg L^{-1} (equivalent to 0, 0.5, 1, 2, 4, 10, 20, and 40 µg of arsenic, respectively) were added to 60-mL polyethylene bottles, each containing 0.5 g of soil. The final volume in each bottle was adjusted to 20 mL using deionized water. The extent of arsenic adsorption varied among soils and was primarily influenced by clay content; soils with higher clay content exhibited greater arsenic adsorption. The adsorption data conformed well to the Langmuir adsorption isotherm, particularly at lower concentrations of arsenic, indicating monolayer adsorption behavior. The efficiency of arsenic extraction using a phosphate buffer also varied across soils. The phosphate extractant was able to remove between 19% and 95% of the adsorbed arsenic, suggesting that this fraction may be available for plant uptake.

Keywords: Adsorption isotherm, arsenic, soil

1. Introduction

Arsenic contamination in groundwater poses a serious threat to human health, agricultural productivity, and environmental sustainability in Bangladesh. This contamination affects 61 out of 64 districts, with approximately 60% of the country's land area impacted by elevated arsenic levels (Joarder *et al.,* 2001). Naturally occurring arsenic has also been detected at high concentrations in both groundwater and soils (Panaullah *et al.,* 2003).

The mobility and solubility of arsenic in the soil solution are largely governed by the physical and chemical properties of soils, which influence arsenic adsorption–desorption dynamics. Adsorption of arsenic by soil plays a crucial role in limiting its bioavailability to plants and, consequently, its entry into the food chain. Soils with higher arsenic adsorption capacity can reduce arsenic solubility and restrict its leaching to groundwater.

Although extensive research has been conducted on metal adsorption in pure silicate and oxidic mineral systems, comparatively little information is available on arsenic adsorption and transport in natural soils. Studies with model systems indicate that arsenic exhibits a strong affinity for oxidic surfaces; however, the reactivity of these oxides can vary significantly depending on soil pH, surface charge density, and the composition of the soil solution (Smith *et al.,* 1995; Hira *et al.,* 2023). Other key factors influencing arsenic adsorption include soil texture (Wauchope, 1975; Frost and Griffin, 1977), mineral composition (Walsh *et al.,* 1977; Pierce and Moore, 1980), pH, and the presence of competing ions. Given the widespread occurrence and toxicity of arsenic, understanding its adsorption behavior in soils is of critical importance. The present study was undertaken to investigate the adsorption characteristics of arsenic in selected soils from different regions of Bangladesh.

2. Materials and Methods

Eight soils of Bangladesh, 3 from Paba (designated as P-1, P-2 & P-3), 3 from Faridpur sadar (F-1, F-2 & F-3), and 2 from Sonargaon (S-1 & S-2) Upazilas, were used in this study. The soils had varied contents of clay, OM, As, Fe, P, and S. The important soil properties are presented in Table 1. The total arsenic status ranged from 10.8 to 38.2 mg kg^{-1}. An amount of 0.5 g of soil was taken into a series of 60 mL polyethylene bottles. The arsenic solutions at varying levels, viz. 0, 25, 50, 100, 200, 500, 1000, and 2000 µg L^{-1} (i.e., 0, 0.5, 1, 2, 4, 10, 20, and 40 µg) were added to the bottles, and the final volume was made to 20 mL with de-ionized water. The samples were then stirred for 16 h using a horizontal shaker. The suspension was centrifuged at 5000 rpm for 15 minutes, and the supernatant was filtered using a 0.45 µm membrane filter and stored at below 5°C for arsenic analysis (APHA, AWWA, WEF. 2017). The soil remaining in the bottle was shaken with 20 mL of 0.2M phosphate buffer for 24 h and then filtered again with a 0.45 µm membrane filter. The samples were run in triplicate. The amount of arsenic in the soil extract was assessed by FI-HG-AAS (UNICAM 969).

3. Results

The physical and chemical properties of the soils are shown in Table 1. The properties of the soils varied widely: pH 7.5 to 8.4, clay content 16 to 52 %, citrate dithionite extractable Fe (total free FeO) from 3.78 to 12.73 g kg$^{-1,}$ and the oxalate extractable Mn ranging from 7.7 to 22.4 mg kg^{-1}. The total As concentration in soils also had a wide range from 5.3 to 38.2 mg kg^{-1}. The amount of arsenic adsorption varied from soil to soil. Soils F-1 and P-1 had the highest amount (70.6 and 70.5 mg kg^{-1}) of arsenic adsorption, and soil P-3 had the lowest (49.1 mg kg^{-1}) (Fig.1). The clay contents of soil F-1 and P-1 were 40 and 52%, respectively, while P-3 soil had 16% clay content.

An attempt was made to fit the As adsorption data to the Langmuir equation. The following model of the Langmuir adsorption isotherm was followed for the purpose.

C/X/m= 1/kb + c/b

Where, b = adsorption maximum (μg g^{-1}), k = constant related to the bonding energy of As to the soil (ml $μg^{-1}$), c = equilibrium concentration of As in soil solution (μg ml^{-1}), X/m= amount of As adsorbed per unit weight of soil (μg g^{-1}). A plot of C/X/m versus C was made for each of the eight soils (Fig. 2). The Langmuir plots of As adsorption data exhibit a curvilinear tendency. The fit was better when the curves were split into two linear portions. Such results suggest two different types of adsorption sites for As. The two portions of the curve were considered separately. The lower four points (hereafter referred to as part 1) had a different slope from the upper four points (hereafter referred to as part 2). The correlation between C vs C/X/m was better in part 1 than in part 2, indicating that the Langmuir equation holds best for lower concentrations of adsorbent.

Table 1. Important properties of soils under study

Soil ID	pH	Clay (%)	OM (%)	P	S	Mn	As (total)	Fe
				(mg kg^{-1})				(g kg^{-1})
P-1	8.1	52	4.7	7.50	14.45	10.8	10.8	5.96
P-2	7.7	32	2.8	21.23	7.91	8.5	13.2	5.70
P-3	8.4	16	2.1	32.81	15.12	7.8	23.6	3.78
F-1	7.6	40	2.9	38.60	12.93	14.4	38.2	12.73
F-2	7.6	18	2.7	38.35	19.72	18.3	27.9	8.12
F-3	7.6	24	2.7	56.12	0.64	17.6	36.9	11.94
S-1	7.5	25	2.3	15.32	19.71	7.7	7.2	5.53
S-2	7.8	29	1.7	14.05	12.52	22.4	5.3	7.62

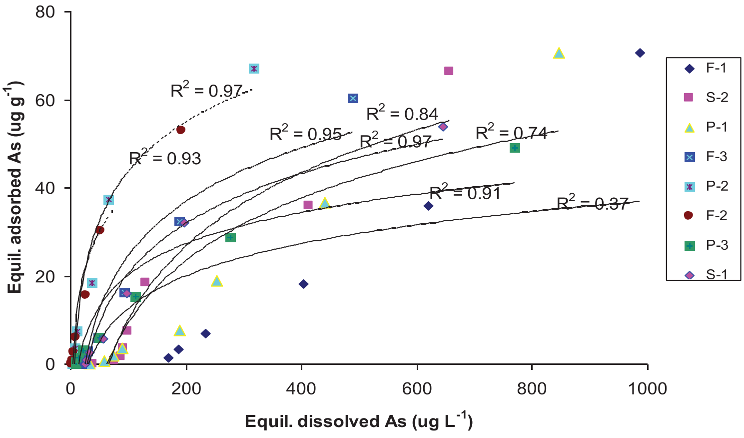

Fig. 1 Adsorption isotherm of arsenic by soil

Table 2. Correlation matrix of soil properties and arsenic adsorption parameters

	pH	**Clay**	**OM**	**P**	**S**	**Fe**	**Mn**	**As**	**b**	**K_1**	**K_2**
pH	1.00										
Clay	0.04	1.00									
OM	0.16	0.78^{**}	1.00								
P	-0.24	-0.47	-0.23	1.00							
S	0.10	-0.09	-0.03	-0.48	1.00						
Fe	-0.58^{*}	0.16	0.03	0.65^{*}	-0.47	1.00					
Mn	-0.33	-0.09	-0.25	0.29	-0.21	0.59^{*}	1.00				
As	-0.16	-0.18	0.03	0.92^{**}	-0.36	0.72^{*}	0.21	1.00			
B	-0.31	0.79^{**}	0.43	0.23	-0.77^{**}	0.72^{*}	0.53	0.27	1.00		
K_1	-0.04	0.10	0.14	-0.35	-0.30	-0.45	-0.35	-0.48	0.06	1.00	
K_2	0.57	0.21	-0.05	-0.56	0.15	-0.61^{*}	-0.59	-0.46	-0.29	0.36	1.00

b= maximum adsorption capacity
K_1=energy of adsorption in part 1 from Langmuir adsorption isotherm
K_2=energy of adsorption in part 2 from Langmuir adsorption isotherm

Table 3. Langmuir coefficients and correlation between C and C/X/m

Soil ID	Part 1			Part 2		
	b_1 (ug g^{-1})	K_1 (mL ug^{-1})	r_1	b_2 (ug g^{-1})	K_2 (mL ug^{-1})	r_2
P-1	2.06	972.6	0.925**	68.52	2.90	0.915**
P-2	1.72	2907.5	0.953^{**}	63.69	3.74	0.849**
P-3	1.83	288.3	0.877*	40.48	3.74	0.999**
F-1	2.25	-494.8	0.996**	68.49	2.81	0.961**
F-2	1.23	406.5	0.947**	50.00	1.56	0.942**
F-3	1.18	651.5	0.954**	57.50	1.33	0.960**
S-1	1.54	721.7	0.981**	44.25	2.59	0.973**
S-2	1.89	586.8	0.902**	67.57	2.90	0.987**

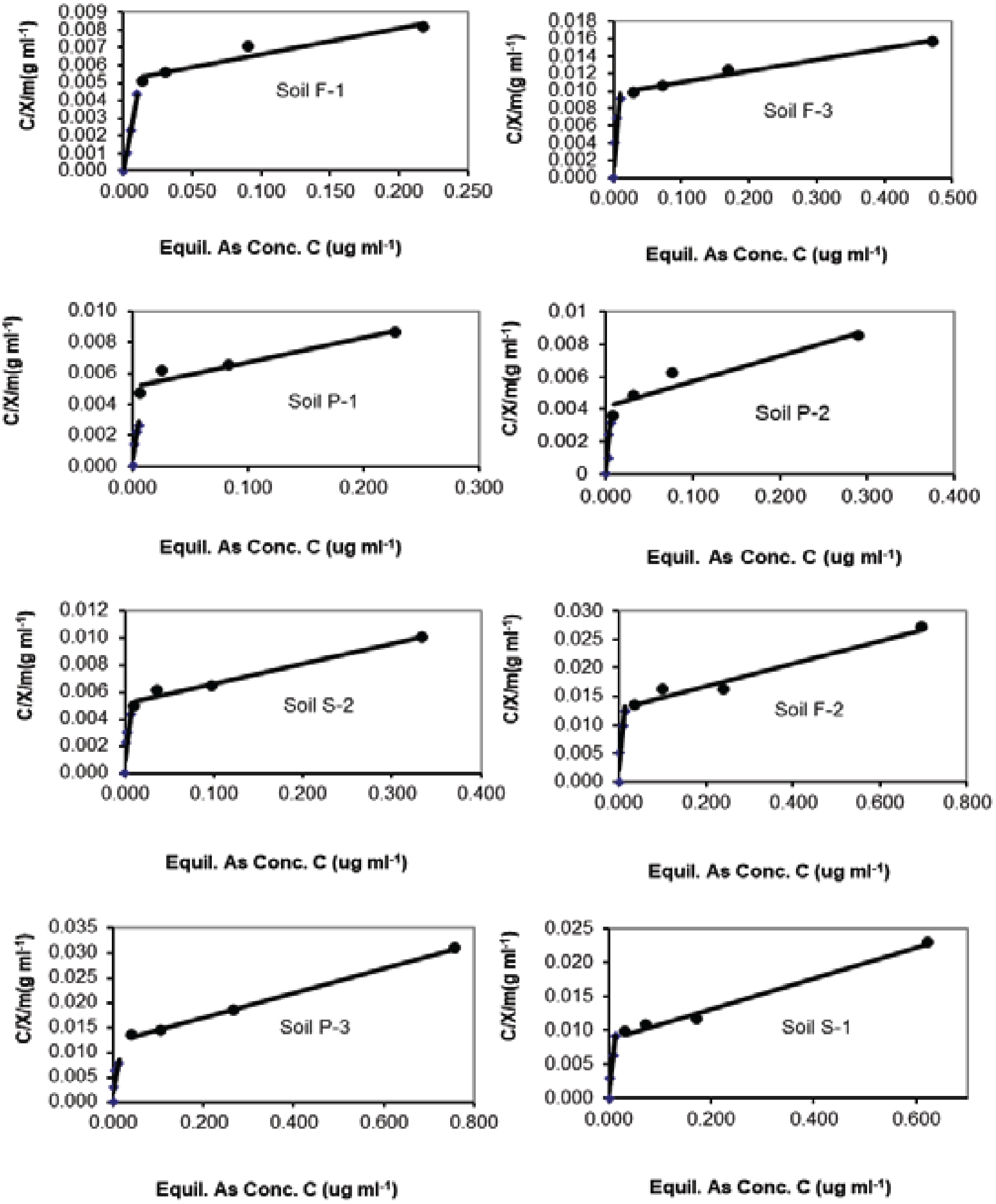

Fig. 2 Langmuair adsorption isotherm plot for different soils

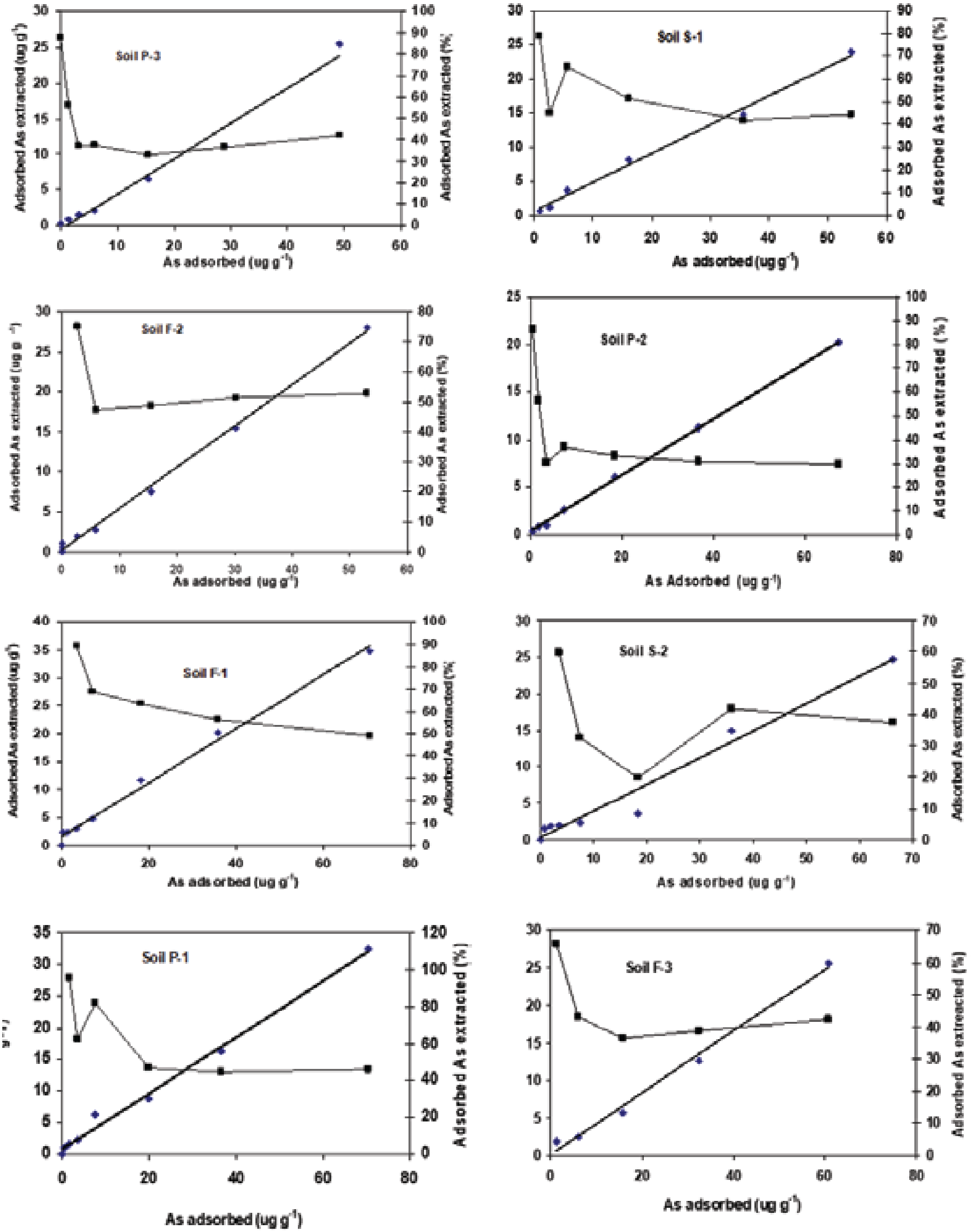

Fig. 3 Phosphate extractable As vs adsorbed As (Axis title is applicable for all of the image)

The Langmuir coefficients were calculated from the equations for the best-fit straight lines following the procedure of Syers *et al.* (1973). The adsorption maximum for part 1 (b_1) was subtracted from all values for part 2, and a new regression for C/X/m vs C was computed. This corrected regression was used to calculate the coefficients for part 2 of the curves (b_2 and k_2). This procedure suggests an evaluation of the part 2 site for their bonding energy and adsorptive capacity without interference from part 1 sites. For all the soils, the adsorptive capacity (b) was higher for the part 2 site, while the bonding energy was higher for the part 1 site (Table 3). Such a result suggests that there are two kinds of adsorption sites differing in the extent to which they adsorb As and in bonding energies. The adsorption maxima b was statistically correlated with clay content ($r= 0.79$, $p \leq .01$). Saleq et al. (2003) reported that As adsorption followed the Langmuir isotherm and the adsorption maxima correlated with clay content. The values for k_1 indicate that the sites in part 1 (k_1) have a much greater affinity for As than those in part 2 (k_2). It can be shown that k_1 must be appreciably greater than k_2 to obtain the sharp breaks in the Langmuir isotherm, as obtained in Fig. 2. The remarkably uniform values for k_2 (Table 3) may suggest that the sites involved in the sorption of added As in part 2 are qualitatively similar.

The phosphate extractable As removed from adsorbed As also varied from soil to soil. The phosphate extractant removed 19 - 95 % of adsorbed arsenic from the soil (Fig. 3). The highest removal of As adsorption occurred from P-1 soil (95.3%), followed by F-1 (89.5%), and the lowest amount was removed from S-2 soil (59.2%).

4. Discussion

The total As in the investigated soils showed a significant correlation with available P and total free FeO. The variation in arsenic adsorption onto soils can be attributed to the variation in clay contents; the higher the clay content, the higher the adsorption. The clay content of the soil showed a strong positive correlation with adsorbed As. Because the adsorption of material is directly proportional to the specific surface areas (Tan, 1998, Khan, S., *et al.* 2023), and clays have a higher surface area, which supports the results. The adsorption maxima of As by soil showed a negative correlation with pH and $CaCl_2$ extractable S, while organic matter, $NaHCO_3$ extractable P, and total free FeO had a positive correlation with adsorption maxima of As (Table 2). Livesey and Huang (1981) reported that P significantly suppressed the sorption of As by competing as $H_2PO_4^-$ (Tiberg et al., 2020; Gustafsson, J.P. and Antelo, J. 2022). The phosphate extractant removed 19 - 95 % of adsorbed arsenic from the soils (Fig. 2), which is expected to be available for plant uptake. The extraction efficiency of phosphate buffer for As varied with soils and also with increasing arsenic additions.

5. Conclusion

Clay content was identified as the primary factor influencing the variation in arsenic adsorption among the soils. The efficiency of adsorbed arsenic extracted by phosphate buffer showed a decreasing trend with increasing levels of arsenic addition.

Conflict of Interest

The authors declare no conflicts of interest regarding publication of this paper.

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