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## ADSORPTION OF ARSENIC (As) IN SOILS AND IN THEIR CLAY FRACTION

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### Abstract

Adsorption of arsenic by three soils and their clay fractions were studied separately in order to evaluate their potential in reducing arsenic mobility and bioavailability, and the possible application of this technique for the remediation of soils contaminated with arsenic. The soil series selected were Ghior (high clay content), Ghatail (medium clay content) and Rajoir (organic soil). The maximum amount of arsenic was adsorbed by Ghior soil, followed by the Ghatail soil while the minimum was adsorbed by the organic soil, the Rajoir soil. Variations in adsorption of As among soils were attributed to the content and nature of the clay fractions, presence of organic matter, iron content and magnitude of CEC. A positive relationship ( $r = 0.9079$ ) was noticed between the adsorption of arsenic and clay content of the soils. A fairly noticeable inverse relationship was observed between the adsorption of arsenic and organic matter ( $r = -0.9577$ ), Fe content ( $r = -0.8584$ ) and cation exchange capacity ( $r = -0.9316$ ) of the soils. Adsorption of arsenic by clay fractions of the corresponding soils showed somewhat similar trend to that of the adsorption of arsenic by soils. The extent of adsorption appeared to have varied with the variation of mineral types in the clay fractions of the soils. The illitic minerals present in the clay fractions were probably mainly responsible for the adsorption of arsenic.

### Introduction

At present serious arsenic contamination of drinking water has been reported from various countries of the world, including Bangladesh,<sup>(1)</sup> the West Bengal region of India,<sup>(2,3)</sup> South-Western Taiwan,<sup>(4,5)</sup> Inner Mongolia, China,<sup>(5-7)</sup> and Vietnam.<sup>(8)</sup> Elevated concentrations of arsenic in drinking water have resulted in symptoms of chronic arsenic poisoning in local populations.

Arsenic is the major contaminant of groundwater in Bangladesh. The source of arsenic is geogenic and hosted by the sediments in the Holocene alluvial low lands.<sup>(9,10)</sup> Since arsenic is a natural part of our environment, everyone is exposed

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to some amount of arsenic. One of the potential exposure pathways to As ingestion is through the food chain where arsenic contaminated groundwater is used for irrigation and there is a possibility for increased concentrations of the element in soils.<sup>(11)</sup>

Remediation methods currently used to treat soils contaminated with arsenic are expensive, labor-intensive and environmentally invasive. They are mainly based on civil engineering, techniques often involving excavation and removal of contaminated soil with additional effort, time and money required to restore the site. A low cost remediation technique that is environmentally sound, and equally protective of human health and the environment, would be a valuable and viable alternative to current remediation methods. Research has been directed towards exploiting biological and chemical process to reduce the risk associated with the arsenic contaminated soils. The use of soil amendments to alter the chemical and physical form of arsenic contaminants in the environment, thus decreasing chemical and biological activity, shows promise; inactivation whether or not combined with phytostabilization, is for stabilizing trace elements that are potentially toxic. This should result to an attenuation of the impact of site and adjacent ecosystem.

Easily available and inexpensive amendments, such as natural soils and clay fractions separated from those soils can be easily used. These amendments do not produce drastic changes in the physical, biological or chemical properties of the soils. Another important advantage of this technique is that the soil is not excavated and amendments could be applied on a large scale. Clay minerals are ubiquitous in soils and altered rocks, hence are inexpensive. They are non-toxic; they have high surface areas and commonly carry permanent negative charges leading to a high CEC. Some swell in water. As a result of these properties, they are useful for minimizing the bioavailability of metal contaminants.<sup>(12)</sup>

With these views in mind the present work was undertaken to investigate the adsorption of arsenic by several soils of Bangladesh and the clay fractions of these soils as potential binding agents for the remediation of the polluted soils.

## **Materials and Methods**

Two mineral soils and one organic soil were used in the present research work. The soils were collected from three districts (Mymensingh, Madaripur and Gopalganj) of Bangladesh. The soils collected represent the Ghatail (Mymensingh), Ghior (Madaripur), and Rajoir (Gopalganj) series. After collection, the soils were air-dried and ground to pass through a 2-mm sieve. The bulk sample was thoroughly mixed and stored. Particle size analysis (Table 1) was performed by

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hydrometer method as described by Day.<sup>(13)</sup> The textural class (Table 1) was determined by following Marshall's triangular co-ordinates as designed by USDA.<sup>(14)</sup>

Soil pH (Table 1) was measured by a combined electrode pH meter at a soil : water ratio of 1 : 2.5 as suggested by Jackson.<sup>(15)</sup> Cation exchange capacity (CEC) was determined (Table 1) by using neutral 1N NH<sub>4</sub>OAc saturation technique.<sup>(16)</sup> The soil organic matter (Table 1) was estimated by Walkley and Black's wet oxidation method as outlined by Jackson.<sup>(15)</sup> The total nitrogen content (Table 2) of the soils was determined by alkali distillation of the Kjeldhal digest.<sup>(15)</sup> Moreover, the total content of K, Ca, Mg, Fe and P in the soils (Table 2) were determined by using prescribed laboratory methods as outlined by Jackson.<sup>(15)</sup>

**Table 1. Properties of the selected soils.**

Soil series	pH	OM (%)	Sand (%)	Silt (%)	Clay (%)	Textural class	CEC meq/kg	Clay minerals <sup>(20,21)</sup>
Ghior	6.48	0.29	1.7	14.1	84.2	Clay	408.5	Ill, Kt, Mont, Vt, Ct, Qz, Fd.
Ghatail	6.33	0.5	4.5	39.9	55.6	Clay	322	Kt, Ill, Mont, Vt, Ct, Qz, Fd.
Rajoir	4.81	19.75	71.7	10.9	17.4	Sandy loam	867.1	Kt, Ill, Mont, Vt, Ct, Qz, Fd.

CEC = Cation exchange capacity, Kt = Kaolinite, Ill = Illite, Mont = Montmorillonite, Vt = Vermiculite, Ct = Chlorite, Qz = Quartz, Fd = Feldspar.

**Table 2. Total content of N, K, Ca, Mg, Fe, P and As (both aqua regia extractable and water soluble) of the soils studied.**

Soil series	N (%)	K (%)	Ca (%)	Mg (%)	Fe (%)	P (%)	As mg/kg	
							Aqua regia extractable	Water soluble
Ghior	0.1	0.7	24.9	5.05	2.16	0.06	0.35	n.d.
Ghatail	0.15	0.26	6.1	3.79	2.8	0.052	0.29	n.d.
Rajoir	1.52	.057	5.32	1.54	3.34	0.021	4.5	n.d.

n.d. = Below detectable limit of the apparatus.

The soil arsenic was extracted by aqua-regia (3 : 1, HCl : HNO<sub>3</sub>). The samples were digested for approximately 4 - 5 hours, using a sand bath as a heating source and the water soluble As was extracted by shaking 10 g samples of soil with 50 ml distilled water for 24 hours. After dissolution, samples were diluted to volume, mixed and filtered prior to analysis.<sup>(17)</sup> Then the arsenic in the extracts (Table 2) was estimated by Hydride Generation-Atomic Absorption Spectrophoto-

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meter (HG-AAS) with the help of potassium iodide (KI) and urea following calibration of the equipment. With every set of digestion a certified reference material (CRM) was included to ensure the QA/QC.

Soil clay fractions were separated by the method of Kunze<sup>(18)</sup> and Jackson.<sup>(19)</sup>

The following two groups of potential adsorbent materials were selected for the As adsorption test:

Soils (Ghatail, Ghior and Rajoir): On the basis of their clay content.

Clays (Separated from the selected soils).

Solutions for batch tests with concentrations ranging between 0 and 10.0 mg/l arsenic were prepared with de-ionized water from NaAsO<sub>2</sub>. The pH of the soil suspensions was adjusted to 6.0 using HCl or 0.1M NaOH.

Adsorption tests were carried out in centrifuge tubes by shaking a given dose of adsorbent with 25 ml of solution on a vertical rotary shaker (50 turns/min) in a chamber set for two hours and were allowed to equilibrate at a constant temperature (22 ± 0.5°C) for 24 hours. The suspensions were centrifuged at 1800 rpm over one hour and filtered. Arsenic concentrations in the supernatant were determined with a Varian Spectraa-220 HG - AAS. All assays were carried out in triplicate and only mean values are presented (the variation coefficients were less than 5%). Adsorption by soil/clay (X) was calculated by deducting the value of As in the equilibrium solution (C) (supernatant) from the value of As (C<sub>0</sub>) in the solution. 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:

$$X = \frac{V_0 C_0 - V_1 C_1}{W}$$

where,

X = amount of As adsorbed (mg/kg soil),

V<sub>0</sub> = initial volume of As solution (ml),

C<sub>0</sub> = initial concentration of As solution (mg/l),

V<sub>1</sub> = total volume of equilibrating solution (ml),

C<sub>1</sub> = final concentration of As in equilibrating solution (mg/l),

W = weight of soil taken.

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The following form of the Langmuir adsorption isotherm was tested to calculate the adsorption coefficients:

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

Where,

$C$  = equilibrium concentration of As in solution (mg/l),

$X$  = amount of As adsorbed (mg/kg),

$b$  = adsorption maximum (mg/kg),

$k$  = constant related to the bonding energy of As to the soil(mg/kg).

A plot of  $C/X$  versus  $C$  was made for each of the three soils. The values of adsorption maximum and bonding energy were calculated from slope ( $1/b$ ) and intercept ( $1/kb$ ) of the plot, respectively.

A comparative study of arsenic adsorption capacity on the different soils and their respective clays were carried out separately with the following conditions: Adsorbent dose: 1 g soil/0.1g clays in every 25 ml solution, shaking time 2 hours, pH-6, the initial arsenic concentration were 0, 0.25, 0.50, 1.0, 2.0, 5.0 and 10.0 mg/l.

## Results and Discussion

*Arsenic adsorption on soils:* Equilibrium solution arsenic concentrations ( $C$ ) and amounts of arsenic adsorbed ( $X$ ) at various initial arsenic solution concentrations ( $C_0$ ) are presented in Fig. 1.

The adsorption of arsenic varied amongst the soils as well as with the initial solution concentrations, which ranged from 0 to 10 mg/l. The lowest value (6.2 mg/kg soil) was observed for all soils at 0.25 mg/l and the highest adsorption of 193 mg/kg soil was observed for Ghior soil at 10 mg/l. It was thus observed that Ghior soil adsorbed the highest amount of arsenic amongst the soils studied. For all soils, arsenic adsorption increased with increasing rate of arsenic addition.

The  $b$  values (adsorption maximum) for the soils studied as presented in Table 4 followed the order: Ghior > Ghatail > Rajoir. The values of adsorption maximum increased with increased clay content and with decreased organic matter and Fe content in the soils (Fig. 2). Considering the  $b$  parameter of the Langmuir equation, it was observed that the soils with the highest cation exchange capacity showed the lowest adsorption capacity for arsenic (Table 4). The bonding energies for arsenic represented by  $k$  (Table 4) were different for the soils. When the capacity to adsorb arsenic was high, the energy with which it was held is high.

Arsenic adsorption varied from soil to soil depending on certain dominant properties. In general, the absolute values of adsorption maximum were different. However, the observed wide variations in the adsorption maximum and bonding energy of arsenic between soils are attributable to the content and nature of clay fraction, organic matter content and Fe content. The Langmuir model provided a useful insight into the adsorption of arsenic by the soils. (Fig. 3).

**Table 3. Mineralogical properties of the soils.**<sup>(20,21)</sup>

Soil series	Kt (%)	Ill (%)	Mont	Vt	Ct	Qz	Fd
21 Ghior	20-40	40-60	5-20%	Trace	Trace	Trace	Trace
21 Ghatail	20-40	20-40	Trace	5-20%	Trace	Trace	Trace
20 Rajoir	20-30	15-30	Trace	Trace	Trace	Trace	Trace

Kt = Kaolinite, Ill = Illite, Mont = Montmorillonite, Vt = Vermiculite, Ct = Chlorite, Qz = Quartz, Fd = Feldspar.

**Table 4. Correlation between C/X and C and Langmuir coefficients for soils/clays.**

Arsenic source	Soil series	b (mg/kg)		k (mg/kg)		r	
		Soil	Clay	Soil	Clay	Soil	Clay
Sodium meta arsenate (NaAsO <sub>2</sub> )	Ghior	201.92	534.84	1.92	0.49	0.86*	0.88**
	Ghatail	186.31	299.43	1.49	1.55	0.90**	0.99***
	Rajoir	164.50	270.16	1.20	1.19	0.92**	0.99***

\*, \*\*, \*\*\* indicate significance at 5, 1 and 0.1 per cent confidence level, respectively.

*Arsenic adsorption on clays:* Adsorption varied in the clay materials separated from the three soils. The clays showed similar trends as for the whole soils; *i.e.*, Ghior > Ghatail > Rajoir. The mineral composition of the clays might have played a role in the sorption process.

Table 3 shows the semi-quantitative mineral composition of the selected soil clays. Comparative study of the arsenic adsorption tests of the different types of clays selected permits the classification of the clays in the following order according to their arsenic adsorption capacity (from maximum to minimum) Ghior > Ghatail > Rajoir. The equilibrium solution arsenic concentrations and amounts of arsenic adsorbed by soil clays are presented in Fig. 4.

The adsorption of arsenic varied amongst the soil clays as well as with the initial solution concentrations, which ranged from 0 to 10 mg/l. The lowest value 39.3 mg/kg clay was observed for Rajoir clay at 0.25 mg/l and the highest adsorption of 484.48 mg/kg was observed for Ghior clay. As with arsenic adsorption by whole soils (previous section), it was thus observed that Ghior clay

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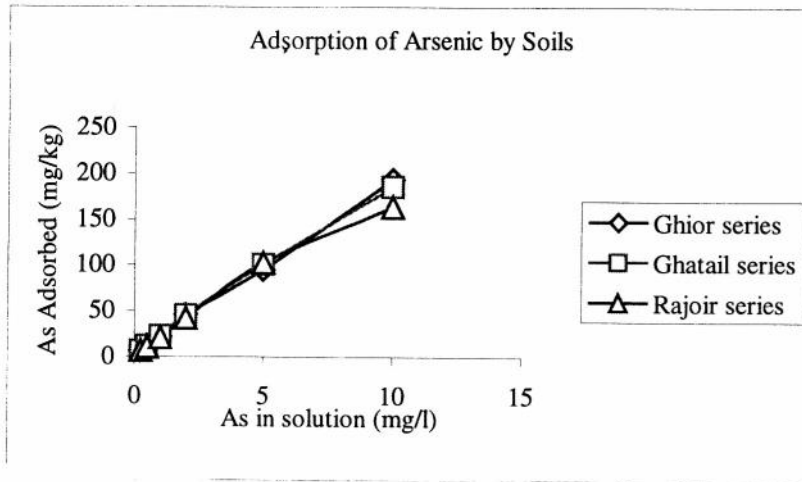


Fig. 1. Arsenic adsorption isotherms for soils.

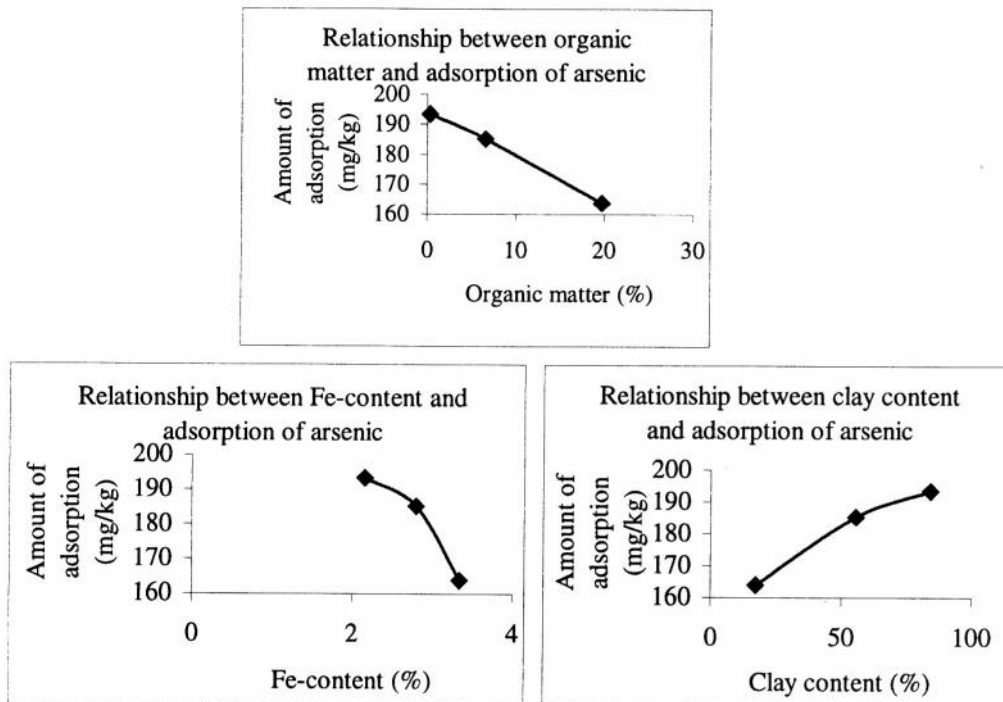


Fig. 2. Relationship between clay content, organic matter and Fe-content with adsorption of arsenic.



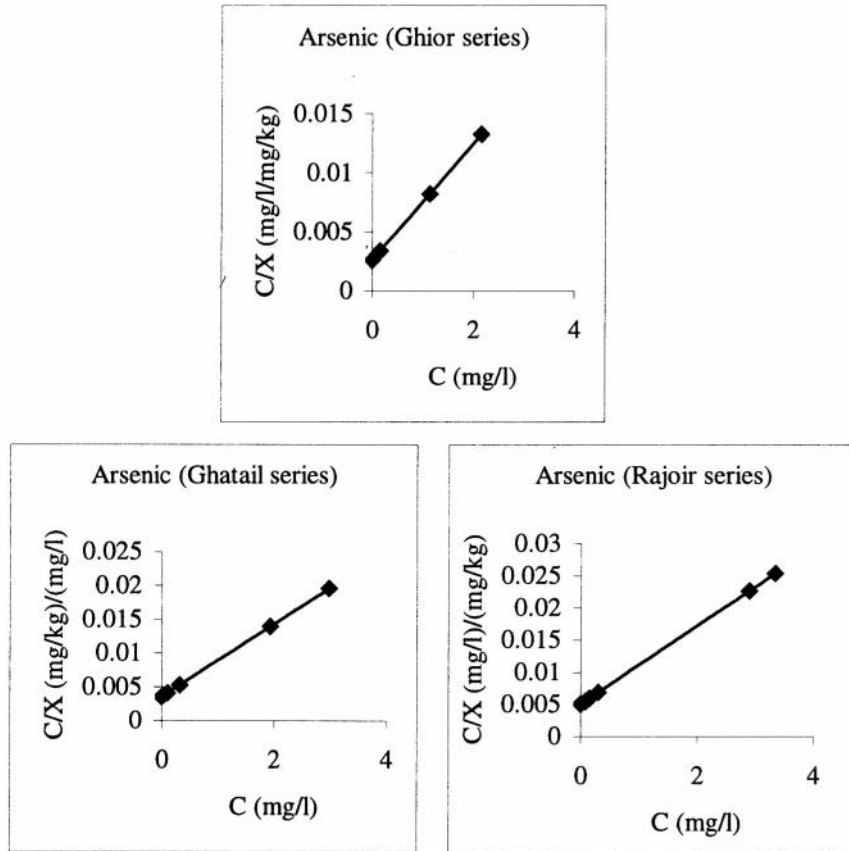


Fig. 3. Langmuir adsorption plots for soils (Arsenic).

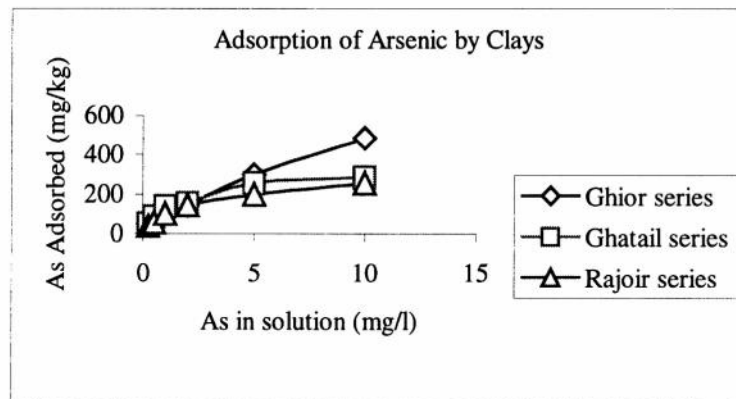


Fig. 4. Arsenic adsorption isotherms for soil clays.



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adsorbed the highest amount of arsenic amongst the clays studied. For all clays, arsenic adsorption increased with increasing rate of arsenic addition. The difference in adsorption by clays at the same initial concentration was probably due to the mineralogy of the soil clay fractions as they contained variable proportions of clay minerals, having different surface characteristics and charges. The  $b$  values (adsorption maximum) for soil clays as presented in Table 4 followed the order: Ghior > Ghatail > Rajoir. The values of adsorption maximum increased

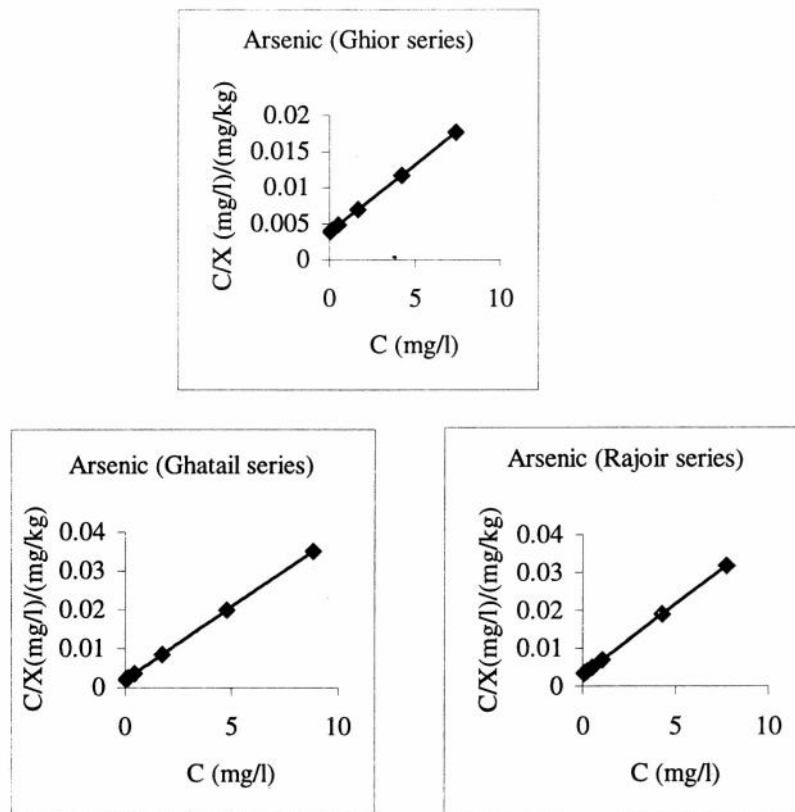


Fig. 5. Langmuir adsorption plots for soil clays (Arsenic).

with increased proportion of illite minerals in the clays. This is evident by the fact that clay of Ghior series, containing more than 50% illite, have  $b$  values of 534.84 as compared to the values of 299.43 and 270.16 observed for soil clay of Ghatail series and Rajoir series which contained less than 40% and less than 30% illite, respectively. This is also evident that clays containing more kaolinite adsorbed more arsenic (higher  $b$  value) than that of clays containing less amount of kaolinite. Besides, clays that showed higher adsorption capacity (higher  $b$  value) also contain a small amount of montmorillonite. Arsenate can be adsorbed onto

clays especially kaolinite and montmorillonite.<sup>(22,23)</sup> Soil clays containing some montmorillonite partly accounted for their high *b* values.<sup>(24)</sup> When the surface area of the clay was higher then the adsorption of arsenic was higher.<sup>(25)</sup> In this work the clays containing higher surface area adsorbed higher amounts of arsenic (as the clay containing higher percentage of illite and montmorillonite contain higher specific surface area than that of clays containing kaolinite). The adsorption data obtained for higher concentrations fitted as well as for the data obtained for lower concentrations. The bonding energies for arsenic represented by *k* (Table 4) were different for the soil clays. Arsenic adsorption data for the soil clay fraction conformed to the Langmuir adsorption isotherm because the fit is excellent (Fig. 5). The observed variation in the adsorptive capacity and bonding energy for arsenic on soil clays indicated the influence of the mineralogy of the clays. The clay content and the nature of minerals present should be considered when predicting the arsenic adsorptive capacity of a soil and clarifying interaction of arsenic and geomaterial.

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