**ARSENATE AND ARSENITE ADSORPTION IN RELATION WITH CHEMICAL PROPERTIES OF ALLUVIAL AND LOESS SOILS**

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 *Abstract*: Arsenic is one of the most toxic elements in soil environment. Understanding of arsenic adsorption chemistry is essential for evolving the extent of soil and ground water contaminations. This research was conducted to determine the variation in adsorption behavior of arsenite and arsenate with depth in different lithology soils. We sampled two parent materials at genetic horizons, and within a parent material we selected two soils. Besides basic soil characterizations, a laboratory batch experiments were carried out to study the adsorption of arsenate and arsenite. Freundlich adsorption approaches were employed to investigate the adsorption of arsenate and arsenite in the soils. Freundlich isotherms fit arsenate and arsenite sorption data well with r2 values of 0.88-0.98 in most soils. Arsenate and arsenite adsorption varied with soil properties especially clay content and oxides of iron and aluminum. Arsenic adsorption parameters also varied with depth in parent materials, and loess derived soils had greater adsorption capacity as compared to alluvial soils in most of the adsorption parameters. This research concludes that loess soils had high arsenic adsorption capacity than the alluvial soils.

*Key words*: Arsenic species; parent material; Freundlich isotherms

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RUNING TITLE: ARSENATE AND ARSENITE ADSORPTIONPARAMETERS

INTRODUCTION

Arsenic (As) is one of the most toxic trace element present in soil and water. Naturally As occurs in rocks and mineral weathering can contaminate soil and ground water.1 Anthropogenic activities including application of agricultural pesticides, industrial waste and land filling of sewage sludge contribute As to soil and As mineral weathering. Mineralization of organic matter and cyclic oxidation-reduction release As in soluble form into the soil immediately after addition.2

Arsenic forms a variety of inorganic and organic compounds in soils.3 Inorganic As occurs dominantly as pentavalent arsenate (As(V)) and trivalent arsenite (As(III)). Arsenate species is predominant over As(III) and organic As and it may be up to percent of total As content in contaminated soils.4 The inorganic As phases are hundreds time more toxic than organic phases; and among the inorganic As forms As(III)s are twenty five to sixty times more toxic than As(V).5, 6 Therefore, the correct estimation of As form in soil is important for understanding bioavailability of As and its effects on biota.7

Adsorption is probably the initial As adsorption on metal oxides especially iron oxides i.e. goethite, lepidocrocite and less crystalline ferrihydrite. A large portion of As becomes adsorbed with metal oxides and only a small portion which remains in soil water.8 Arsenic adsorption process controls the toxicity, fate, mobility and bioavailability of As in soils. Soil solution As can be significantly different although the same amount of As is applied to different soils due to its adsorption with soil matrix. Therefore understanding of adsorption of As is important for predicting As behavior in the soil environments.9

Arsenic adsorption on clay, metal oxides of iron and aluminum and organic matter is generally the most common process for As solid phase formation.10, 11 It is well reported that oxides and hydroxides of iron and aluminum are major constituents which controls As adsorption in soils.12, 13 Calcite possibly have role in the retention and solubility of arsenic in carbonate rich environment. Phosphate, organic matter and clay contents are the two important soil factors significantly affect the adsorption of As in soils.14, 15

Arsenate and As(III) adsorption studies used variety of adsorbents such as metal oxides, clays and soils. Studies was conducted on As(V) and As(III) adsorption by amorphous iron and aluminum oxides, and clay minerals i.e. kaolinite and montmorillonite.16 For modeling As(V) and As(III) adsorption most widely used analytical isotherms are Langmuir isotherm17 and Freundlich isotherms.18 Studies on arsenic adsorption in relation with lithology and development are scarce. We hypothesized that adsorption behavior of As(V) and As(III) may vary with soil lithology and within a same lithology parent material, soil development controls the arsenic forms adsorption. We sampled two parent materials at genetic horizon level, and we selected two soils in each parent material. The objectives of the study were to evaluate the adsorption behavior of As(V) and As(III) of different parent materials soils and effect of soil properties on As(V) and As(III) adsorption.

EXPERIMENTAL

SOIL SAMPLING AND CHARACTERIZATION

Soils were taken from the Pothwar Plateau having different parent material and we selected alluvium and loess parent material for the present study. The GPS location and USDA taxonomy of selected soils is given in Table 1. Triplicate profile for each soil was dug and soil samples were taken from each of the genetic horizon. Samples were air dried and crushed to pass through a 2-mm sieve.

 Table 1. Selected soils loess and alluvium parent materials

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| --- | --- | --- | --- |
| Soils | Location  | USDA Classification | Parent Material |
| Rawal | 33o38’46.28’’N and 73o04’57.82’’E | Fine silty, mixed, hyperthermic Typic Hapludalfs | Alluvium |
| Kotli | 33o37’11.13’’N and 73o42’53.92’’E | Fine, mixed, hyperthermic Entic Chromostert |
| Guliana | 33°33’22.12’’N and 72°38’30.82’’E | Silty, mixed, thermic Udic Haplustalfs | Loess |
| Mansehra | 34o24’56’’N and 73o14’06’’E | Fine loamy, mixed hyperthermic Typic Hapludalfs  |

Each sample was analyzed for texture, pH, Calcium carbonat (CaCO3), cation exchange capacity (CEC), Na2S2O4-extractable Fe and Al, and dissolved organic carbon (DOC). The soil particle size distribution was determined by dispersion in (NaPO3)6 solution and soil pH of saturated soil paste was measured. Soil CaCO3 was determined by acetic acid consumption.19 The DOC was extracted with K2SO4 and determined by consumption of K2Cr2O7.20 Soil iron (Fed) and aluminum (Ald) oxides were dissolved in Na2S2O4 and C6H5Na3O7 and NaHCO3 buffer solution. The concentrations of Fe and Al in the extracts were measured by ICP-MS.21 Cation exchange capacity was determined by saturating soil with an index cation.22 Amorphous iron (Feo) and aluminum (Alo) were determined by extracting soil in acidified ammonium oxalate solution in dark.23

BATCH EXPERIMENT FOR ARSENATE AND ARSENITE SORPTION

Sorption isotherms for As(V) and As(III) were constructed to estimate Langmuir-model and Fruendlich model parameters employing the batch sorption experiments.24, 25 Triplicate, three g soil was equilibrated with 30 mL 0.01 M KNO3 solutions containing graded concentration of As(V) 0, 0.1, 2.5, 5, 8, 10, 15, 20, 25, 40 and 100 mg L-1 (Na2HAsO4). The suspension was shaken for 48 h at room temperature and centrifuged for 20 min at 3000 rpm. The supernatant was filtered through 0.45 µmcellulose membrane and analyzed for total arsenic. Separately, three g soil was equilibrated with 30 ml of 0.01 M KNO3 solution containing graded concentration of As(III) 0, 0.1, 0.5, 1, 3, 5, 7 and 8 mg L-1 from NaAsO2. The suspension was shaken for 48 h at room temperature and centrifuged for 20 min at 3000 rpm. Cellulose membrane of 0.45 µm was used to filter the supernatant and total arsenic was analyzed in the extract. Sorbed amountof As(V) and As(III) was calculated from the change in the solution phase concentration.

The adsorption isotherm was fitted to the Freundlich equation.26

 ** [1]

or rearranged in linear form:

  ** [2]

where *x/m* is the equilibrium concentration adsorbed by the soil (mg kg-1), *cw* is the equilibrium concentration in solution (mg L-1), *β* is an adsorption exponent related to adsorption intensity and *Kf*is the Fruendlich adsorption coefficient (L kg-1). A plot of log *x/m* versus log *cw* was fit with using linear regression; *β* was found by the reciprocal of the slope of the regression line. The intercept of this regression line yielded *Kf.*

CHEMICAL ANALYSIS

 pH of soil samples and samples run for CaCO3 were determined by using Cole Parmer pH meter. For CEC analysis NH4+ determination was carried out using shimadzu UV-VIS spectrophotometer. Elemental analysis of Fe, Al, and total arsenic were determined by using PerkinElmer’s ICP-MS.

STATISTICAL ANALYSIS

The variance in the adsorption parameters were ascribed to soil parent material at different depths. The multivariate analysis was implemented using Proc General Linear Model in SAS version 9.4 (SAS Institute Inc., 2014).27 The parent material and soil (parent material) were class variable and the soil depths were multiple dependent variables. Stepwise multiple regression analysis was to correlate adsorption parameters and soil properties that determine adsorption of As(V) and As(III) in soils derived from loess and alluvium.

RESULTS AND DISCUSSION

SOIL CHARACTERISTICS

Soils varied in chemical and physical characteristics which are important for As(V) and As(III) adsorption (Table 2). The soils were dominantly silt loam. Overall, the alluvium derived Kotli soil had larger clay content followed by the Guliana, Mansehra and Rawal soils. Clay leaching and accumulation caused by soil development processes was observed in Bt horizon of all the soils except for the Kotli developed in clayey parent material. Most soils were non-calcareous with lower DOC. Rawal soil under forest conditions showed higher DOC content. Dissolved organic carbon varied in most soils with higher contents in surface horizons and decreased with depth in all the soils due to accumulation of organic material at the surface horizons. Most of the soils were non-calcareous except for the Rawal soil which had CaCO3 in the range of 35 to 100 g kg-1 and increased with depth. Similar values for CaCO3 were reported earlier.28 Cation exchange capacity was in the range of 10 to 30 cmol+/kg. Higher CEC was observed in the Guliana soil with increasing trend with depth and seemed to increase at Bt horizon level in all the soils. Citrate bicarbonate-

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Table 2. Chemical properties of studied soils

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Horizon  | Depth  | pH | Clay  | CaCO3  | CEC  | DOC  | Fed | Ald |  | Feo | Alo | Total As |
|  | cm |  | g kg-1 | g kg-1 | cmol+/kg  | mg kg-1 | -------------------------------g kg-1--------------------- | mg kg-1 |
| Rawal: Fine silty, mixed, hyperthermic, Typic Hapludalfs |  |
| A | 0-10 | 7.05 | 190 | 34(5.27) | 9(0.60) | 300(1.23) | 5.0(0.33) | 1.3(0.08) |  | 0.10(0.02) | 0.62(0.02) | 3.52(0.05) |
| Bw | 10-18 | 7.35 | 215 | 35(3.50) | 12(2.37) | 170(0.40) | 6.6(0.40) | 1.7(0.10) |  | 0.09(0.04) | 0.82(0.07) | 3.40(0.10) |
| Bt | 18-30 | 7.57 | 265 | 53(6.57) | 14(1.19) | 180(0.55) | 9.4(0.33) | 2.5(0.10) |  | 0.09(0.00) | 1.06(0.01) | 3.57(0.13) |
| Bk | 30-46 | 7.63 | 215 | 102(24.7) | 10(1.45) | 160(0.41) | 8.8(0.38) | 2.3(0.06) |  | 0.03(0.02) | 0.83(0.04) | 3.97(0.07) |
| Kotli: Fine, mixed, hyperthermic Entic Chromostert |  |
| Ap | 0-10 | 7.93 | 345 | 5.9(0.30) | 17(0.24) | 150(0.78) | 4.9(0.05) | 1.4(0.02) |  | 0.40(0.12) | 0.69(0.04) | 4.17(0.09) |
| Bw | 10-18 | 8.40 | 345 | 7.3(0.32) | 16(2.46) | 113(0.10) | 5.8(0.29) | 1.6(0.06) |  | 0.51(0.02) | 0.67(0.04) | 3.75(0.20) |
| C | 18+ | 8.20 | 445 | 5.6(0.24) | 18(0.10) | 46(0.36) | 8.7(0.10) | 2.6(0.02) |  | 0.24(0.04) | 0.79(0.05) | 4.43(0.35) |
| Guliana: Silty, mixed, thermic Udic Haplustalfs |  |
| Ap | 0-10 | 7.70 | 210 | 7.8(0.45) | 26(0.65) | 75(0.24) | 8.0(0.41) | 2.4(0.07) |  | 0.21(0.02) | 0.91(0.02) | 5.21(0.04) |
| Bw | 10-20 | 7.37 | 210 | 7.8(0.70) | 18(0.85) | 70(0.48) | 7.7(0.40) | 2.4(0.10) |  | 0.22(0.05) | 0.96(0.05) | 5.48(0.18) |
| Bt1 | 20-30 | 7.48 | 295 | 6.4(1.05) | 30(0.14) | 60(0.08) | 9.7(0.23) | 3.3(0.06) |  | 0.31(0.01) | 1.25(0.04) | 6.92(0.07) |
| Bt2 | 30-50 | 7.50 | 320 | 6.1(1.35) | 26(1.46) | 60(0.67) | 9.3(0.38) | 3.5(0.15) |  | 0.27(0.01) | 1.39(0.10) | 6.66(0.08) |
| Mansehra: Fine loamy, mixed hyperthermic Typic Hapludalfs |  |
| Ap | 0-20 | 7.00 | 200 | 5.6(1.18) | 17(0.60) | 110 (0.40) | 7.2(0.80) | 2.0(0.62) |  | 0.53(0.03) | 0.91(0.03) | 3.87(0.10) |
| Bw | 20-40 | 7.10 | 200 | 5.2(0.74) | 13(0.60) | 88(0.21) | 5.8(0.29) | 2.5(0.07) |  | 0.56(0.04) | 0.43(0.03) | 3.50(0.05) |
| Bt | 40-70 | 7.08 | 310 | 6.2(0.17) | 22(0.08) | 66(0.75) | 8.7(0.10) | 4.0(0.10) |  | 0.69(0.04) | 1.48(0.06) | 4.73(0.21) |

Legend:CaCO3, Calcium carbonate; CEC, cation exchange capacity; DOC, dissolved organic carbon; Fed, dithionate extractable iron; Ald, dithionate extractable aluminum; Feo, ammonium oxalate extractable iron; Alo, ammonium oxalate extractable aluminum mean of n 3; standard deviation in the parentheses

dithionate extractable iron seems increased with depth in all the soils. Overall, the Guliana soil showed greater amount of Fed due to soil development process which results in iron release from primary mineral. In the Rawal, Guliana and Mansehra soils high Fed content at Bt horizon was due to translocation and accumulation at Bt horizon level. Citrate bicarbonate-dithionate aluminum was greater in the loess derived soils as compared to alluvium derived soils indicating significant change in Ald with change in parent material.29 Citrate bicarbonate-dithionate aluminum seems to be increased with soil depth in all the soils. Loess derived Guliana and Mansehra were highly weathered soils as supported by greater content of Fed and Ald compared to alluvium derived Rawal and Kotli soils. Ammonium oxalate extractable iron also varied with parent material. The loess derived Guliana and Mansehra soils had higher concentration of Feo compared to the alluvial Rawal and the Kotli soils. High Feo was observed in soils at relatively higher stage of development and accumulated in Bt horizon whereas in the Rawal and Kotli soils higher Feo was observed in surface horizons due to less leaching.30 High amorphous iron contents in Mansehra soils may attribute to high rainfall which reduces the crystallinity while dry climate promote crystallinity.31 Ammonium oxalate extractable aluminum was higher in soils at higher stage of development since the weathering processes result in an increase in hydrolytic breakdown and release of iron and aluminum from the primary minerals. Ammonium oxalate extractable aluminumcontent also increased with an increase in the depth. Overall iron and aluminum oxides were present in greater amount as a result of weathering in Guliana and Mansehra soils. Total As content varied between 3.4 to 6.92 mg kg-1 in most soil samples. In almost all the soils total As content increase with depth which may indicate subsurface accumulation.

ARSENATE AND ARSENITE SORPTION ISOTHERM

The isotherms for As(V) and As(III) sorption depict variation in shape of isotherms with variation in soil characteristics (Fig. 1). Overall, As(V) adsorption was greater than As(III). Both As(V) and As(III) had fast rise in sorption with a small increase in concentration in equilibrium solution. Several scientists reported a fast sorption initially and a moderate increase lateral part of the isotherm.9, 18 Maximum sorption increase for As(V) was less than 150 mg kg-1. The Bt horizons, especially in case of the Mansehra and the Guliana soils, had faster adsorption rise compared to Ap and Bw horizons. In case of As(III), where generally the concentration maxima was ≈ 30 mg kg-1 had greater rise in

 Figure 1. Adsorption isotherms for arsenate and arsenite constructed between adsorbed concentrations at ordinate and solution concentration at abscissa in, indicating a fast initial rise especially in case of Bt horizon and the Bk horizon of Rawal had noteable low in adsorption.

adsorbed concentration in case of Bt horizons of all the soils. It appears that clay content had stronger role for adsorption of both As(V) and As(III). Several studies indicated a strong correlation of clay content with the adsorption of As(V) and As(III).32, 33

FREUNDLICH EQUATION SORPTION PARAMETERS

Freundlich equation (Eq. 2) fit the isotherms with most of the r2 > 0.95 (Figure 2). Adsorption of As(V) and As(III) in these soils was well fitted by Freundlich isotherm model34. Maximum average adsorption intensity of As(III) (β) was lower than adsorption intensity of As(V) in most soils while adsorption capacity (*Kf*) was greater for As(V) than As(III). It appears that As(V) had higher adsorption capacity As(III) but with lesser binding intensity most soils. The distribution of β and *Kf* for As(V) and As(III) remained similar with soil depth in both of the parent materials (Figure 3), as the hypothesis of nonsignificant depth × PM interaction was accepted through MANOVA test criteria. Fruendlich adsorption parameters increased with soil depth in loess and alluvium. The loess derived soils had higher adsorption parameters (β and *Kf*) than alluvial soils at all soil depths. Variation in β and *Kf* of As(V) and As(III) with soil depth in each parent material was also remained similar (Table 3).

The adsorption intensity ranged from 1.45 to 2.50 and *Kf* of As(V) ranged from 19 to 75 L kg-1 and. These results are in line with the findings of Roy et al.35, Payne and Abdel-Fattah36 and Zeng et al.37. Arsenate β increased with depth in all the soils with increase in clay content (r 0.48). As β is the intensity of adsorption it is related with the abundance of metal oxides. It was evidenced that As(V) had high affinity for metal oxides from positive correlation of β with Fed (r 0.77), Ald (r 0.80), Feo (r 0.42) and Alo (r 0.71). Similarly, *Kf*, increased with depth with increase in clay content as evidenced by positive correlation with clay (r 0.46). The CEC is largely related to clay content38 because of more exchange sites for adsorption, As(V) *Kf* values positively correlated with CEC (r 0.59). The *Kf* had showed strong relation with iron (Fed (r 0.83) and Feo (r 0.50)) and aluminum (Ald (r 0.89) and Alo (r 0.87)) oxides as increase in As(V) *Kf* and metal oxides with increase in soil depth.



Figure 2. Freundlich equation (Eq. 1) fit for arsenate and arsenite isotherms in the selected soil horizons. Arsenate and arsenite adsorption parameters were calculated from the trendline



Figure 3. Distribution of adsorption parameters (*β* and *K*f) of arsenate and arsenite in each parent material (mean = 6, and bars show standard error).

Table 3. Fitted Freundlich sorption model parameters for arsenate and arsenite of each soil

|  |  |  |
| --- | --- | --- |
| Horizon | Arsenate | Arsenite |
| †*β* | ‡*K*f  | *β* | *K*f  |
|  L kg-1 L kg-1 |
| Rawal: Fine silty, mixed, hyperthermic, Typic Hapludalfs |
| A | 1.43(0.06) | 19(0.34) | 2.20(0.02) | 13(0.36) |
| Bw | 1.88(0.01) | 35(0.55) | 2.93(0.14) | 24(0.70) |
| Bt | 1.82(0.02) | 40(0.62) | 2.77(0.35) | 34(0.80) |
| Bk | 1.91(0.08) | 38(0.76) | 2.82(0.25) | 29(0.10) |
| Kotli: Fine, mixed, hyperthermic Entic Chromosterts |
| Ap | 1.80(0.06) | 35(1.40) | 2.07(0.04) | 32(0.18) |
| Bw | 1.81(0.01) | 36(0.45) | 2.65(0.14) | 32(0.29) |
| C | 2.18(0.05) | 47(1.20) | 3.43(0.21) | 50(1.68) |
| Guliana: Silty, mixed, thermic Udic Haplustalfs |
| Ap | 1.73(0.03) | 34(0.59) | 2.74(0.18) | 27(2.29) |
| Bw | 1.90(0.11) | 37(0.85) | 2.98(0.04) | 27(0.42) |
| Bt1 | 2.03(0.11) | 53(0.50) | 3.43(0.10) | 57(0.58) |
| Bt2 | 2.22(0.02) | 61(1.61) | 3.31(0.13) | 66(0.61) |
| Mansehra: Fine loamy, mixed hyperthermic Typic Hapludalfs |
| Ap | 1.74(0.013) | 36(0.24) | 2.40(0.02) | 27(0.20) |
| Bw | 2.01(0.031) | 42(0.38) | 3.11(0.12) | 37(0.85) |
| Bt | 2.50(0.05) | 75(1.96) | 2.61(0.14) | 76(1.80) |

†*β* adsorption intensity and maximum adsorption capacity ‡*K*f were calculated from the respective regression equation. Value in parenthesis is standard 221 deviation.

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Several studies reported the role or iron and aluminum oxides in the As(V) adsorption.13, 18 Overall, As(V) β and *Kf* were increased linearly with the increase in metal oxide contents. Loess derived Guliana and Mansehra soils which are more weathered soils had greater amount of clay in Bt horizons and ultimately higher iron and aluminum oxides resulted in greater adsorption of As(V) as compared to alluvium derived Rawal and Kotli soils. The adsorption intensity, β ranged from 2.07 to 3.43 and *Kf* ranged from 13 to 76 L Kg-1 and. The adsorption parameters vary widely with the change in soil properties especially due to differences in iron oxides.39 The β showed non-significant relation with the metal oxides indicating weak binding of As(III) on metal oxide surfaces. However, As(III) β was positively related with clay content (r 0.38) and CEC (r 0.36). Adsorption capacity of As(III) was higher in weathered horizons of the Guliana and the Mansehra soils while β values are greater in Bw/Bt horizons of all the soils compared to remaining horizons. The K*f* for As(III) increased with depth in all the soils except for the Kotli soil. Similar values for *Kf* of As(III) were observed by Elkhatib et al.39 in loamy soils. Arsenite *Kf*showed similar behavior as As(V) in positive correlation with Fed (r 0.77), Ald (r 0.87), Feo (r 0.46) and Alo (r 0.82). The Bt horizons of the Guliana and the Mansehra soil had higher *Kf* values due to higher clay and metal oxides content.

PREDICTION OF ADSORPTION PARAMETERS

We selected the soil properties (independent parameters) by stepwise regression maximizing *r*2 and predicted the adsorption parameters of As(V) and As(III) obtained from fitting the isotherm to the Fruendlich equation. Soil was included as an independent parameter. Intercept differed with the soil type in case *r*2 improves significantly due to addition of soil type as variable. The multiple regression equations have more value to understand the processes rather than as predictive tools. The regression equations for As(V) and As(III) adsorption parameters are given in the Table 4. It is apparent that β for As(V) is positively related with Ald while negatively correlated with CEC, CaCO3 andclay confirming the observation of Raven et al. 18 that adsorption intensity was more related to metal oxides. Freundlich coefficient related to adsorption capacity K*f* in all soils was more related to Feo and Alo as compared to Fed and Ald.40. However, β for As(III) suppressed by aluminum oxides (Ald and Alo) whereas increased in the presence of iron oxides and CEC related to clay content.38 The regression equation for As(III) K*f* showed that adsorption capacity of As(III) increases with increase in Ald whereas it was suppressed by increase in CaCO3 and CEC.

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| --- | --- | --- | --- |
| Arsenic form  | Regression Equations |  | *r2* |
| Arsenate | *β* = 3.63 + 12.24Ald - 89.92CEC - 7.76CaCO3 - 0.26Clay | 0.82 |
| Kf = 236.33 + 17.80Feo - 72.44Alo | 0.15 |
| Arsenite | *β* = 1.10 + 0.0055Feo - 0.052Alo - 0.021Ald + 0.23CEC  | 0.57 |
|  | Kf = 21.77 + 8.66Ald - 66.50CEC - 5.21CaCO3 - 0.22Clay  | 0.82 |

Table 4. Regression equations for different properties estimate for each adsorption parameter

CONCLUSION

It is concluded from our results that As(V) adsorption was greater than As(III) in all the soils and varied with the soil properties, among which clay content and iron and aluminum oxides exhibited the most important influence on As(V) and As(III) adsorption. Freundlich isotherms fit As(V) and As(III) sorption data well with r2 values of 0.88-0.98 in most soils. Loess soils had higher adsorption capacity than alluvial soils. Metal oxides and clay content are the major predictor for As(V) and As(III) adsorption parameters. This study will help to understand soil and groundwater contamination phenomena.

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