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EVALUATION OF ADSORPTION PARAMETERS AND CHARGE DENSITIES OF SOME SELECTED SOILS: APPLICATION TO LEAD

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ABSTRACT

An attempt to evaluate adsorption parameters and charge-based densities for Pb is reported in the paper. The method was based on the calculation of Langmuir adsorption maximum (a_{max}), and the bonding energy term (b). The parameters were the outcome of well-established linear relationships of C_e/S versus C_e (C_e , equilibrium concentration and S , amount adsorbed). The use of charge-based sorption density parameter (SD_{CEC}), which expressed the number of accessible charges for Pb adsorption, evidenced the occurrence of two main adsorption phases, characterised by two different slopes. The first ones, varying from 0.536 to 3.144 were suggested to be attributed to 'high attractive sites', whereas the second with slopes from 0.011 to 0.259, probably represented 'low attractive sites'. Charge-based sorption density parameters elucidated more Pb adsorption behaviour than did Langmuir adsorption maximum (a_{max}).

Key words: Lead, adsorption parameters, Langmuir isotherm, charge density

INTRODUCTION

The reaction of metal ions with soil body depends both on the physical and chemical nature of the adsorbing surface and properties of metals. Several studies have been conducted to assess quantitatively and qualitatively the phenomena occurring at the interface aqueous-solid soil phase [2, 3, 4, 5, 8, 15]. Widely reported in the literature procedures for calculating basic sorption parameters, i.e. adsorption maximum, bonding energy term, and others, are quite frequently complex and time-consuming. Simple ways for routine and even prediction

studies in order to evaluate soils potential buffering capacities for metals adsorption are quite inexistent. Therefore, it seems reasonable and helpful to present such an approach.

The aim of the current paper was to outline a simple method for evaluating Langmuir adsorption maximum, bonding energy term and a charge-based sorption density for Pb adsorption of some selected soils.

MATERIALS AND METHODS

Theory outline

The Langmuir equation based on the kinetic theory of gases is extensively used to describe gas adsorption on solids. The same equation often applies to the adsorption of liquids and ions from solutions by solids although the same rigorous, theoretical basis is not as fully developed. As applied to liquids or ions, the following equation is used herein:

$$S = \frac{a_{\max} b C_e}{1 + b C_e}$$

where,

S - amounts of Pb adsorbed ($\text{mmol}_c \cdot \text{kg}^{-1}$),

a_{\max} - adsorption maximum ($\text{mmol}_c \cdot \text{kg}^{-1}$),

b - parameter related to the bonding energy of the adsorbent for the adsorbate ($\text{dm}^3 \cdot \text{mmol}_c^{-1}$),

C_e - equilibrium Pb concentration ($\text{mmol}_c \cdot \text{dm}^{-3}$).

The amount of Pb adsorbed by the soils may be calculated by:

$$S = (C_i - C_e) V / W + CV$$

where,

C_i - initial Pb concentration ($\text{mmol}_c \cdot \text{dm}^{-3}$)

V - volume of the initial solution, dm^3 ,

W - weight of a soil sample, kg,

CV - correction value (amount of Pb extracted by DTPA), ($\text{mmol}_c \cdot \text{kg}^{-1}$),

In its linear form, equation (1) may be rewritten as follows:

$$\frac{C_e}{S} = \frac{1}{a_{\max} b} + \frac{C_e}{a_{\max}}$$

where,

the slope is equal to $\frac{1}{a_{\max}}$ and the intercept (when C_e tends closely to 0) is expressed by $\frac{1}{a_{\max} b}$. The value of the bonding energy term (b) is then calculated from the ratio of the slope and the intercept, and it is equal to

$\frac{\text{slope}}{\text{intercept}}$. It is noteworthy that the calculation of the adsorption maximum (a_{\max}) can involve errors of 50% and more [7] if the isotherm does not have correct Langmuir shape.

Soil analyses and equilibration studies

Four surface soils, namely S_1 , S_2 , S_3 and S_4 (Table 1) were randomly collected from arable areas (20 cm depth). The soil particle size was determined by the Prósński areometric method and textural soil class was established according to Soil Survey Division Staff procedure [19]; organic carbon by the method of Tiurin [12] and soil pH in 0.01M CaCl_2 suspension [14]. Cation exchange capacity (CEC) was determined by a modified Mehlich_{8,2} method [10]. The specific surface area was determined by equilibrating soil samples with ethylene glycol monoethyl ether (EGME) according to Carter et al., [1]. The total and organically bound Pb contents were extracted in *aqua regia* [17] and DTPA [11], respectively.

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Table 1. Some physical and chemical properties of the soils

Soil textural class	Particle size (mm)		pH	Organic carbon (g·kg ⁻¹)	SSA ^c (m ² ·g)	CEC (cmol _c ·kg ⁻¹)	CaCO ₃ (%)	EA ^z , (cmol _c ·kg ⁻¹)
	0.1 - 0.02	< 0.02						
Loamy sand ^a (S ₁)	240	130	5.00	5.61	9.44	5.97	-	2.43
Sandy loam (S ₂)	420	220	6.86	14.94	25.17	13.18	-	0.93
Loamy sand ^b (S ₃)	250	200	7.60	12.05	37.41	15.50	2.15	0.43
Loam (S ₄)	270	420	6.95	18.28	72.03	21.29	-	0.90

^a, ^b: for differentiation; ^c: Specific surface area; ^{*}: not detected; ^z: Exchangeable Acidity.

Equilibration studies were carried out at 20°C with applied Pb concentrations varying from 0.2 to 2.0 mmol_c·dm⁻³ as Pb(NO₃)₂ in 0.01M Ca(NO₃)₂ (background electrolyte). Such a wide range of concentrations of metals was used to cover heterogeneity of soil samples; different duplicated soil/solution ratios of 1/15; 0.3/15; 0.2/15 and 0.15/15 were applied for soils S₁; S₂; S₃ and S₄, respectively. The slurries were agitated for 2 hours and equilibrated for 22 hours. Equilibrium concentrations (*C_e*) as well as total and DTPA extractable Pb were determined by AAS method (Atomic Absorption Spectrophotometry, Varian Spectra 250 plus). The soil solid-phase Pb was calculated as the difference between initial Pb concentrations (*C_i*) and those in solutions after equilibration. Statgraphics and Computations and illustrations were made by using Statgraphics and Excel packages.

RESULTS AND DISCUSSION

Soil samples used in the study differed significantly in their physical and chemical properties (Table 1). For convenience the loamy sand^a, sandy loam, loamy sand^b and loam soils will be referred to as S₁, S₂, S₃ and S₄, respectively. Cation exchange capacity (CEC) varied from 5.97 to 21.29 cmol_c·kg⁻¹ with soils representing mostly neutral to basic reaction, except the acidic soil S₁ (pH 5.00). Total lead content of the soils showed a moderate contamination level (0.79 mmol_c·kg⁻¹ or higher) according to IUNG, [9] except for the soil S₃ for with Pb content amounting for 0.18 mmol_c·kg⁻¹ (Table 2).

Table 2. Total and DTPA lead content of the soils (mmol_c·kg⁻¹)

Soil textural class	Total Pb	DTPA Pb	Labile Pb [*] (%)
Loamy sand ^a (S ₁)	1.78	0.51	28.7
Sandy loam (S ₂)	1.23	0.27	22.0
Loamy sand ^b (S ₃)	0.18	0.02	11.1
Loam (S ₄)	0.79	0.09	11.4

^{*}: quotient of DTPA-Pb to Total-Pb multiplied by 100.

a. Graphical evaluation of Pb sorption parameters

Metal-ion binding by natural particles is expected to be a highly nonlinear process and should therefore be dependent on the absolute concentrations of a given metal in the surrounding solution. Lead affinity to soil solid-phase surfaces was found to be notably different depending on several factors such as metal properties. The values of adsorption maxima and bonding energy terms for Pb are reported in Table 3. As it could be observed, the calculation of these parameters was facilitated by the graphical presentation of the plots of *C_e/S* (i.e. equilibrium to adsorbed Pb) versus *C_e* (equilibrium Pb) typical for the Langmuir isotherm (Fig. 1, Fig. 2, Fig. 3 and Fig. 4). The resulting straight lines were the requisite conditions for calculating the adsorption maximum (*a_{max}*) and the bonding energy term (*b*) that derived from the slopes and intercepts, respectively, as reported in Equ. 3. This is important, since serious deviation from linearity may generate results burdened with 50% errors, or even higher as reported by Harter [7]. The soil solid-phase formation of Pb may be strictly related to its chemistry on one hand and the soil medium, on the other. If we restrict soil properties to organic matter, clay and carbonates content, reflecting the relative magnitude of soils buffering properties expressed by their CEC, then the values of *a_{max}*, *b* and *MBC* seem to prove geochemical specificity of Pb adsorption by soils. According to Santillan-Medrano and Jurinak [16] lead reaction in slightly calcareous soils is very effective with a resultant of mixed compounds such as PbCO₃, Pb(OH)₂, typical for chemisorption. It seems consistent with the following order expressing the relative degree of CEC saturation (*a_{max}*/CEC):

$$105\% (S_3) > 100\% (S_4) > 73\% (S_2) > 30\% (S_1)$$

Table 3. Adsorption parameters calculated from the plots of C_e/S versus C_e for Pb of the Soils.

Soil textural class	Slope	Intercept	a_{max}^x ($mmol_c \cdot kg^{-1}$)	b^y $dm^3 \cdot mmol_c^{-1}$	MBC^z ($dm^3 \cdot kg^{-1}$)	R^2
Loamy sand ^a (S ₁)	0.0564	0.00631	17.73 ± 0.76	8.94 ± 0.38	158.50 ± 6.79	0.997
Sandy loam (S ₂)	0.0104	0.00011	96.15 ± 16.05	94.54 ± 15.13	9090.02 ± 1569.35	0.993
Loamy sand ^b (S ₃)	0.0062	0.00015	161.29 ± 46.71	41.33 ± 7.67	6666.12 ± 1448.01	0.964
Loam (S ₄)	0.0047	0.00029	212.76 ± 64.96	16.20 ± 4.33	3446.71 ± 1017.97	0.911

^x: adsorption maximum; ^y: bonding energy term; ^z: maximal buffering capacity ($a_{max} \cdot b$).
 *: mean values and standard deviation; R^2 : coefficient of determination.
 More details see "Materials and Methods" and Figs. 1.

Figure 1. Langmuir isotherm for Pb adsorption by the soil S₁

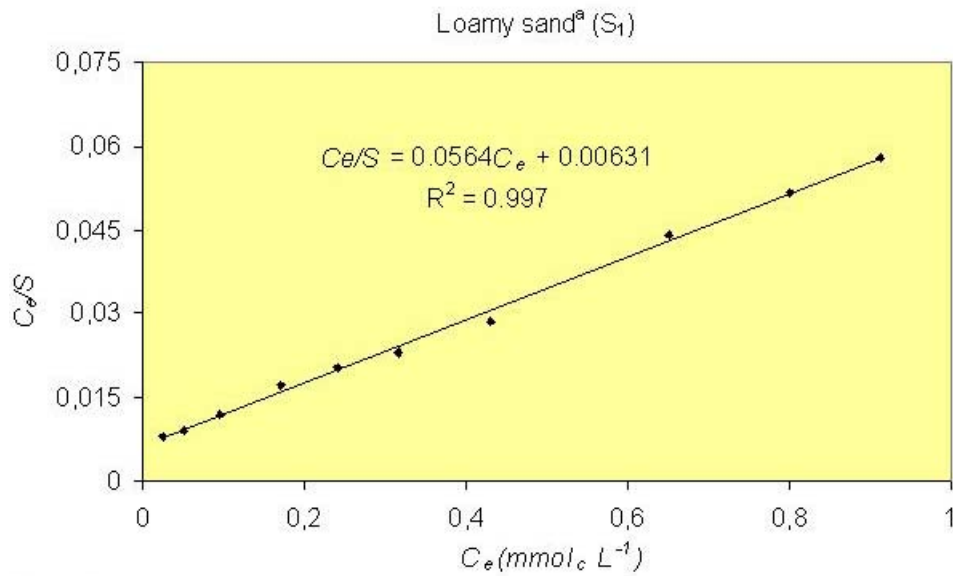


Figure 2. Langmuir isotherm for Pb adsorption by the soil S₂

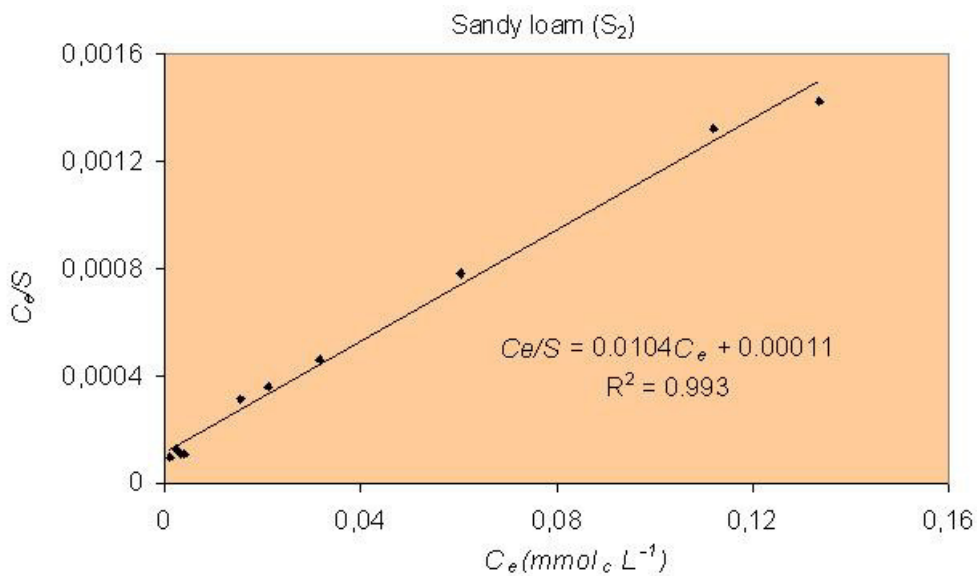


Figure 3. Langmuir isotherm for Pb adsorption by the soil S₃

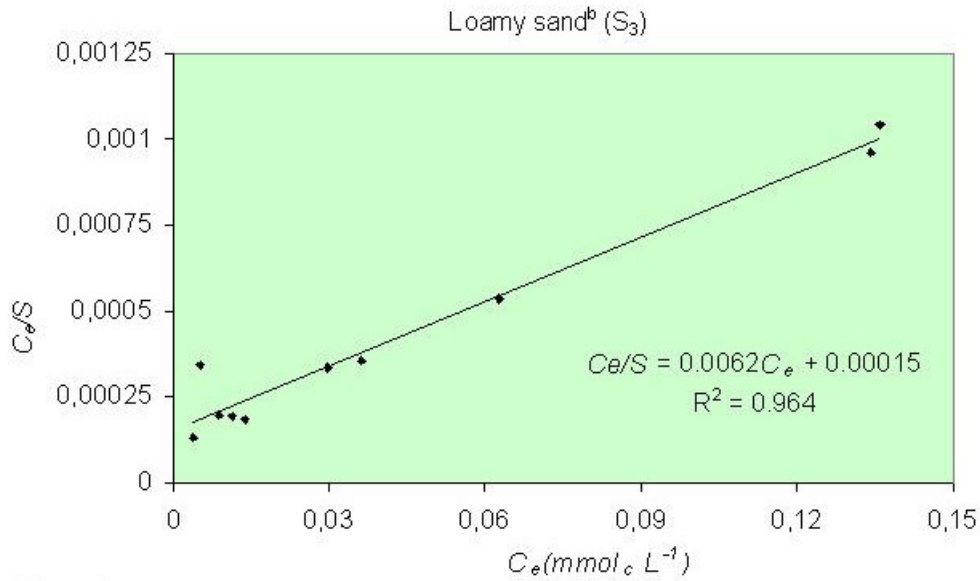
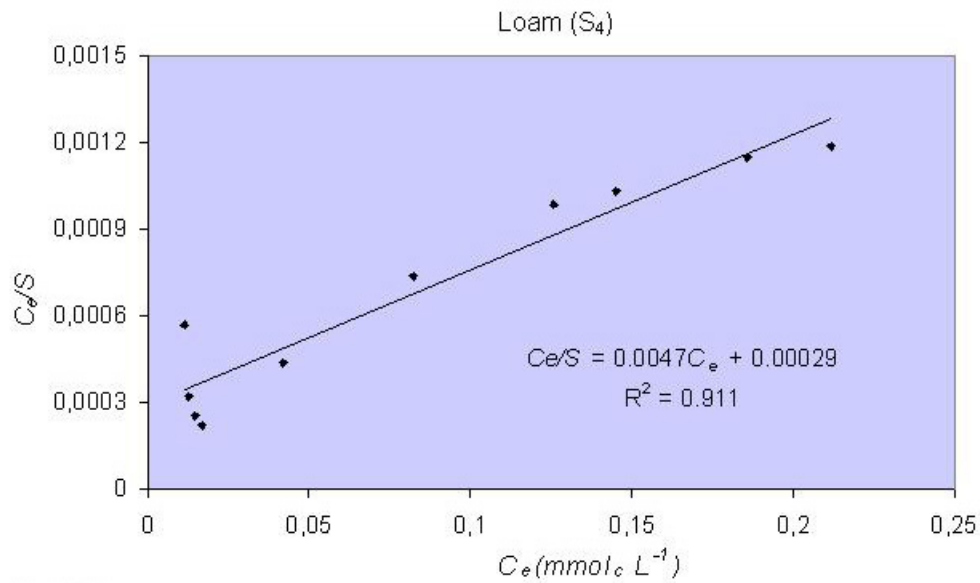


Figure 4. Langmuir isotherm for Pb adsorption by the soil S₄



Oversaturation of CEC in soil S₃ most likely originated from occurrence of carbonates, which in turn led both to Pb adsorption and precipitation resulting in formation of stable soil complexes, as reported by Sposito et al. [20] and Elkhatib et al. [4]. The suggested method to evaluate adsorption maximum (a_{max}) gave reliable results irrespective of soil types. The magnitude of a_{max} values was found to conform the order observed for the specific surface area, (SSA) and the cation exchange capacity, (CEC).

b. Lead sorption densities approach

Sorption processes, especially nonspecific adsorption, are greatly influenced by the surface charge of which cation exchange capacity (CEC) is a measure. Amounts of lead adsorbed in the CEC may be expressed as ions per moles of charge, including thus a charge-based sorption characteristics. Such charge-based sorption density, SD_{CEC} as suggested by Schulte and Beese [18] and Zehetner and Wenzel [24], was adapted for Pb as follows:

$$SD_{CEC} = \frac{(CV + S) N_A}{CEC}$$

where,

SD_{CEC} - charge-based sorption density, (ions·mol⁻¹),

N_A - Avogadro's number, (6.023×10^{23} ions·mol⁻¹).

The relationships between Pb solution concentrations and their corresponding charge-based sorption densities presented in Fig. 5, Fig. 6, Fig. 7 and Fig. 8, suggest the use of the sorption densities as a mean of evaluating quantity-intensity relationships of Pb in soils. Affinity of Pb towards negatively charged CEC-sites may be assessed with satisfactory accuracy. For example, at equilibrium concentration, C_e of $5.0 \mu\text{mol}_c\text{dm}^{-3}$ the charge-based sorption densities (SD_{CEC}) for Pb will amount to 1.6×10^{22} ; 20.3×10^{22} ; 15.1×10^{22} and 0.52×10^{22} ions·mol⁻¹ for soils S₁; S₂; S₃ and S₄, respectively. SD_{CEC} of soils S₂ and S₄ deserve additional consideration due to inflection of the lines. Proper inflection points represented equilibrium concentrations of $C_e = 4.07$ and $16.98 \mu\text{mol}_c\text{dm}^{-3}$ corresponding to SD_{CEC} of 16.79×10^{22} and 24.49×10^{22} ions·mol⁻¹ for soils S₂ and S₄, respectively. With further additions of Pb behind the inflexion point, the increase of SD_{CEC} values was relatively low in comparison with the ones recorded for Pb levels up to the inflection point. Such slight increase of SD_{CEC} may be attributed to the occurrence of new population of sorbing sites characterized by weak attraction energies. This is consistent with the findings of Msaky and Calvet, [13]; Basta and Tabatabai, [2] who reported high affinity of soils for copper at low concentration, which decreased with further increase of concentration.

Figure 5. Isotherms of the sorption density (SD_{CEC}) vs equilibrium concentration (C_e) for the soil S₁

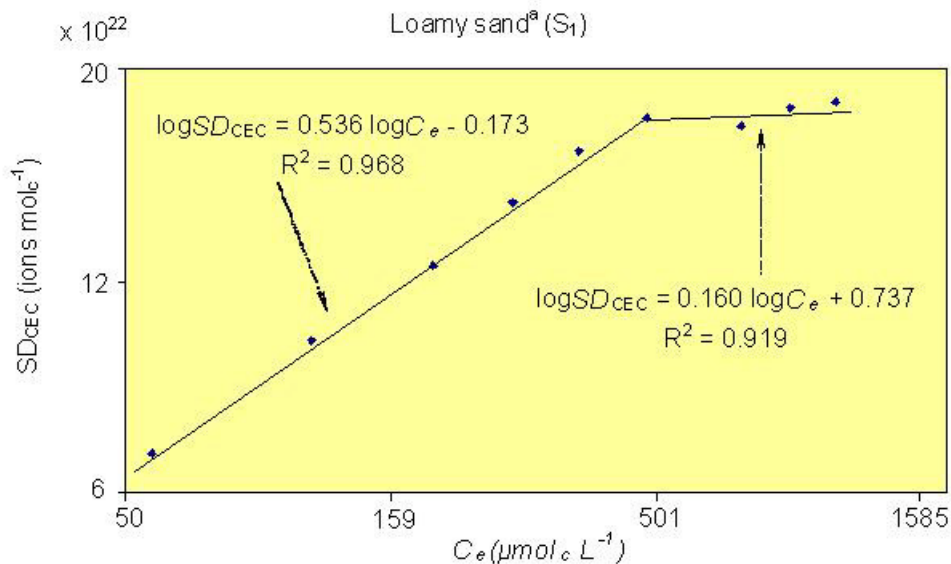


Figure 6. Isotherms of the sorption density (SD_{CEC}) vs equilibrium concentration (C_e) for the soil S₂

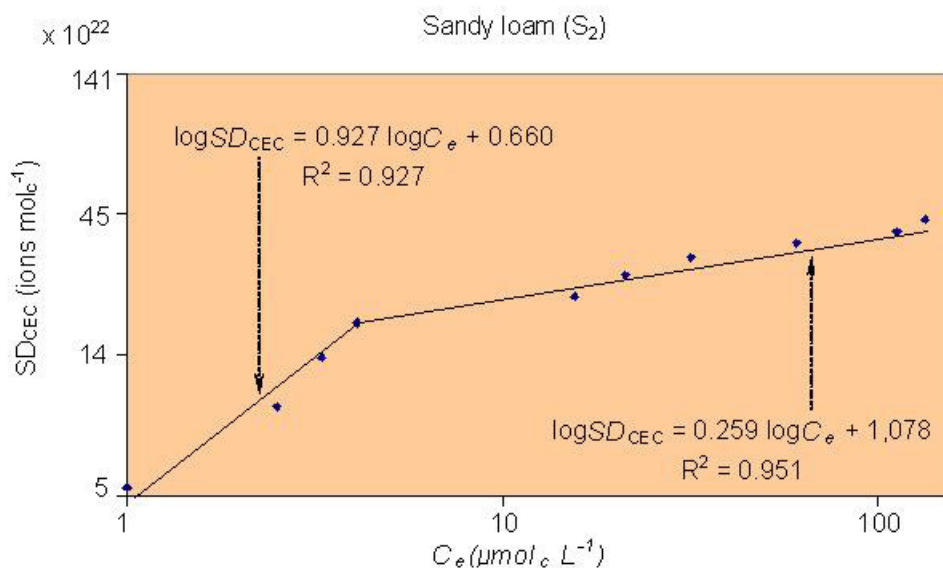


Figure 7. Isotherms of the sorption density (SD_{CEC}) vs equilibrium concentration (C_e) for the soil S_3

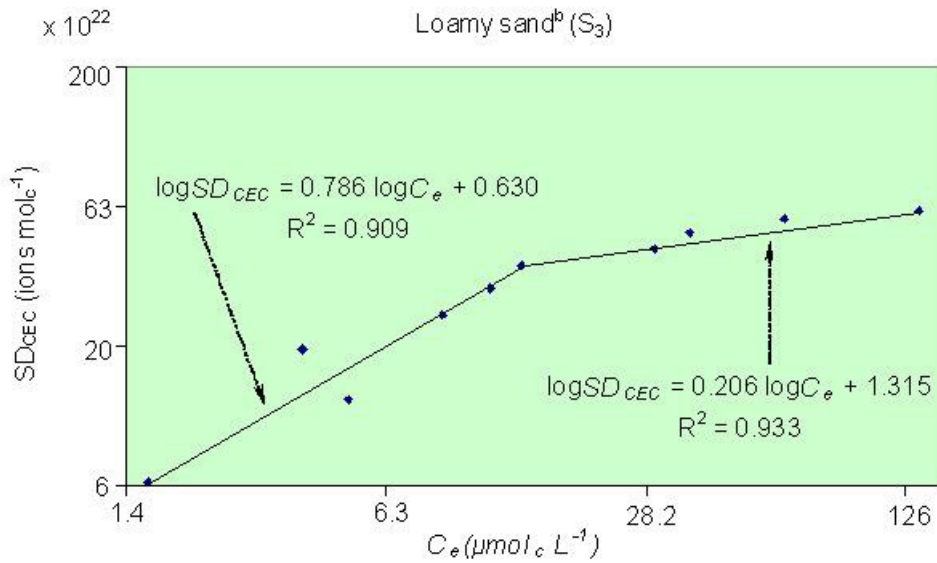
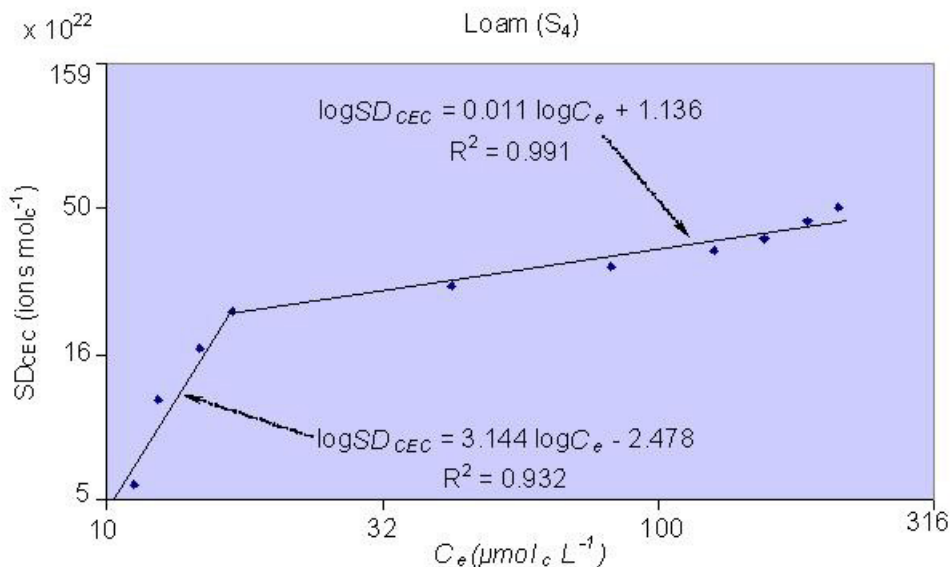


Figure 8. Isotherms of the sorption density (SD_{CEC}) vs equilibrium concentration (C_e) for the soil S_4



Furthermore, it is noteworthy to point out the L-type linear shapes [6; 22] of Pb charge-based sorption density isotherms of the soils. The Langmuir one-site isotherm is conceptually valid for monolayer sorption on a surface containing a finite number of binding sites. Moreover, the treatment assumes uniform energies of sorption on the surface and no transmigration of adsorbates into the plane of the surface. Such restrictions are not applicable to solids characterised by heterogeneous adsorptive surface like those found in soil systems. Data analysis and interpretation based solely on Langmuir adsorption maximum (a_{max}) should be undertaken with care since it does not outline some sorption particularities as illustrated in [Fig. 5](#), [Fig. 6](#), [Fig. 7](#) and [Fig. 8](#). Interestingly, SD_{CEC} values did not follow the order observed both for the specific surface area (SSA) and cation exchange capacity (CEC) as listed in [Table 1](#). Lead was adsorbed basically at two types of sites represented by two straight lines: the first is indicative of energetically high sites with a relatively high slope, whereas low energetic sites appeared in the second range being characterized by a decreasing slope. Therefore, the isotherms are in agreement with occurrence of heterogeneous adsorption surface which consisted of adsorption sites of high and low energy [20; 23]. On the basis of the slopes, the soils may be ranked as follows:

High energetic sites:

$$S_4 (\text{slope} = 3.14) > S_2 (0.93) > S_3 (0.79) > S_1 (0.54)$$

Low energetic sites:

$$S_2 (\text{slope} = 0.26) > S_3 (0.21) > S_1 (0.16) > S_4 (0.011)$$

The observed ranks, both for high and low charge distribution showed that the sorptive complex of investigated soils can not be restricted to a single adsorption parameter. Furthermore, as clearly evidenced by relationships between SD_{CEC} and Pb equilibrium concentration, Pb adsorption expressed in terms of charge-based density could be used as a simple and efficient parameter for accurate evaluation of soil capacity for Pb adsorption. The approach may be of practical use also for ecotoxicology assessment.

CONCLUSIONS

1. Well-defined linear relationships between C_e/S and C_e are prerequisite conditions for Langmuir adsorption parameters (a_{max} and b) calculation.
2. Occurrence of carbonates may enhance Pb adsorption leading thus to an “oversaturation” of the sorptive complex as a result of chemisorption.
3. Expressing lead adsorption in terms of charge-based sorption density allowed deeper insight into the adsorption process than offered by Langmuir adsorption maximum approach.
4. All investigated soils were characterized by a two-phase adsorption process. The mechanisms involved stressed evidence of both high and low adsorption sites.
5. Evaluation of adsorption parameters, as outlined herein, seems to be easily applicable and may provide valuable information about adsorption processes.

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