Comparative effects of the sorption of cadmium in organic and kaolinitic soils

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Abstract: This research has investigated and compared, through batch tests, the influence of the addition of bentonitic material and organic matter on the delay process of cadmium migration in the environment. In addition the work has also studied the parameters of sorption by analyses of isotherm curves. For this, four different materials were mixed in the laboratory to form two blocks of samples, each one containing five "sub samples" prepared with different ratios of the initial samples. The first comprised a mix of a soil that represents the geochemistry of most tropical soils (composed predominantly of kaolinite) and bentonitic material, acquired locally. The second comprised a mix of kaolinite and an organic horizon obtained from a tropical soil. The "sub samples" were composed of the following ratios, respectively: 1 (100% Soil / 0% Adsorbent), 2 (75% / 25%), 3 (50% / 50%), 4 (25% / 75%) and 5 (0% Soil /100% Adsorbent). Clay fractions of each soil were collected by sedimentation at times prescribed by Stokes law. Analysis of the kaolinitic soil indicated the presence of kaolinite, illite and goethite; analysis of the bentonitic material smectite, trace amounts of illite and kaolinite; analysis of the kaolinite pattern only kaolinite and finally, the organic horizon which recorded trace amounts of illite and interstratified illite-smectite. Batch tests were carried out with cadmium solutions, prepared at four different concentrations (500, 1000, 1500 and 2000 ppm). The data were analyzed by means of atomic absorption and the sorption isotherms were plotted based on models of Langmuir and Freundlich. The Langmuir model was found to provide the best fit to the analysed data based on the correlation coefficients. After this procedure, the retardation factors were determined. The results show that the proportion of bentonitic material and organic horizon in a soil sample significantly affect the cadmium retention. The most sorption was found to occur on soils composed entirely of the organic horizon.

Résumé: Cette recherche a pour objectif de faire des recherches et des comparaisons, au moyen d'essais d'équilibre en lot, l'influence d'addition de matériel bentonitique et de matières organiques au processus de retard des migrations de Cd dans l'environment. Le travail vise aussi a étudier les paramètres du sorption par le moyen d'analyses des courbes isothermes. Pour ça, quatre différents types de sol ont été mélangé au laboratoire, et j'ai géré deux "blocs" d'échantillons, chacun comprenant cinq échantillons qui sont préparés pour differentes raisons avec des matériaux initiaux. Le premier bloc est réalisé par le mélange d'un sol représenté par la géochimie de la majorité des sols tropicaux - constitués par kaolinite et la bentonite a cherché dans le commerce local. Le deuxième est composé d'un mélange de kaolinite et d'un horizon organique superficiel qui a été retiré dun sol tropical. Les échantillons ont eu les résultats suivants, respectivement: 1 (100% sol / 0% de matière adsorbante), 2 (75% / 25%), 3 (50% / 50%), 4 (25% / 75%) et 5 (0% soil /100%). La fraction argile de chacun des sols a recueilli pour sédimentation ets besée sur début de la Loi de Stokes. Le sol caolinitique a presenté kaolinite, illite, goethite; la matière bentonitique a presenté smectite, quelques illite; et mélange de kaolinite a presenté seulement kaolinite et enfin, l'horizon organique a presenté quelques illite et interstratification de illite-smectite. Des essais par lots ont été effectués avec quatre concentrations différentes avec des solutions de 500, 1000, 1500 et 2000 ppm de Cd. Les résultats sont analysés par l'absorbe atomique et les isotermes de sorber ont piloté basée sur modeles de Lagmuir et Freundlich. Selon les coefficients de corrélation, les meilleurs ajustements sont choisis. Après cette procédure, les facteurs de retardement sont determinés. La matière bentonitique ainsi que l'horizon organique sont influencié significativement par la rétention du métal, mais la sorption plus grande s'est produite sur des sols avec l'horizon organique.

Keywords: clay minerals, soils, pollution, environmental geology, and laboratory studies.

INTRODUCTION

With increasing industrialization, technical development and economic growth, the quantity of waste has increased immensely. The reason for this is that industry and society have tended to dispose of their waste with little regard for future consequences. Because of this, the demand for technologies that diminish the environmental impact of soils and waters had also increased (Bell, 1998).

Characterization of a hazardous waste site involves gathering and analyzing data to describe the processes controlling the transport of wastes from the site. The movement of dissolved contaminants is controlled by advection, mechanical dispersion and molecular diffusion. In addition to these processes, the migration of reactive contaminants is further controlled by adsorption, desorption, chemical reactions and biological transformation. Adsorption is generically defined as a soil-pollutant interaction process, in which the pollutant is transferred from fluid to the solid phase (McLean & Bledsoe, 1992).

Adsorption of metal cations has been correlated with soil properties such as pH, redox potential, clay, soil organic matter, Fe and Mn oxides, and calcium carbonate content. Adsorption processes are affected by these various soil factors, by the form of the metal added to the soil, and by the solvent introduced along with the metal. The results of these interactions may increase or decrease the movement of metals in the soil water (McLean & Bledsoe, 1992).

The focus of this research was to investigate and compare, through batch tests, the influence of variations in bentonitic material and organic matter on the sorption and delay processes of cadmium migration in the environment. This subject is of importance to be able to evaluate the amount of contaminant, for example, accidentally spilled over the ground, which could reach the water table in an unconfined aquifer by means of infiltration.

Cadmium may be adsorbed by clay minerals, carbonates or hydrous oxides of iron and manganese or may be precipitated as cadmium carbonate, hydroxide, and phosphate. Evidence suggests that adsorption mechanisms may be the primary source of Cd removal from soils (Dudley *et al.*, 1988, 1991). Cadmium was chosen for this research because it is a component of fungicides that are often spread over the soil surface during agricultural operations. From a toxicological point of view, cadmium is one of the most hazardous metals. It has a very low maximum contaminant level (MCL) in drinking water (10 µg/l) due to its high toxicity (Manahan, 1994). Cadmium is an acute toxin, producing symptoms such as giddiness, vomiting, respiratory difficulties, cramps and loss of consciousness at high doses. Chronic exposure to the metal can lead to kidney disorders, anaemia, emphysema, anosmia (loss of sense of smell), cardiovascular diseases, renal problems and hypertension (Robards & Worsfold, 1991).

METHODOLOGY

Soil Characterization

For this research, four different types of soils were mixed in the laboratory, generating two blocks of samples, each one containing five "sub samples" prepared with different ratios of the initial samples. The first block of samples comprised a mix of a soil that represented the geochemistry of most tropical soils (comprised essentially of kaolinite) and bentonitic material which was acquired locally. A mix of kaolinite pattern and organic material taken from a horizon in a tropical soil constituted the second one. Table 1 presents the "sub samples" weight ratios for the kaolinitic soil, bentonitic material, kaolinite pattern and organic horizon for each sub sample, while Table 2 presents the actual carbon and organic matter contents in the initial soils.

Table 1. Sub samples weight ratios generated in laboratory.

	1st Block		2nd Block	
Soil Mix	**Kaolinitic Soil (%)**	**Bentonitic Material (%)**	**Kaolinite Pattern (%)**	**Organic Horizon (%)**
Sub sample 1	100	0	100	0
Sub sample 2	75	25	75	25
Sub sample 3	50	50	50	50
Sub sample 4	25	75	25	75
Sub sample 5	0	100	0	100

Table 2. Carbon and organic matter contents in initial soils.

Soil Sample	Carbon (%)	Organic Matter (%)
Kaolinitic Soil	0.04	0.07
Bentonitic Material	0.17	0.29
Kaolinite pattern	0.22	0.38
Organic Horizon	9.92	15.39

The clay fraction of each soil sample was collected by sedimentation at appropriate times prescribed by Stokes law. Thin sections were prepared for X-ray analysis in three different conditions: (i) natural state (N), (ii) saturated in an ethylene glycol (EG) atmosphere for 24 hours and (iii) oven heated (H) at 550 °C for 4 hours. Figure 1, Figure 2, Figure 3 and Figure 4 show the X-ray diffraction diagrams for the kaolinitic soil, bentonitic material, organic horizon and for the kaolinite pattern respectively. In the kaolinitic soil, the minerals identified were kaolinite, illite and goethite while the bentonitic material recorded smectite, trace amounts of illite and kaolinite. Figure 4 shows the high quality of the kaolinite pattern, in which kaolinite was the only clay mineral present. This can be compared to the analysis of organic horizon (Figure 3) which recorded trace amounts of Illite and interstratified Illite-Smectite.

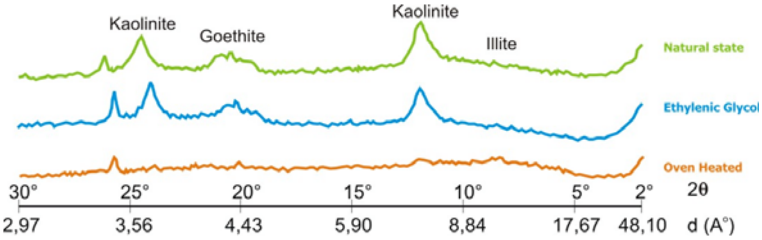

Figure 1. X-ray diffraction diagram for kaolinitic soil.

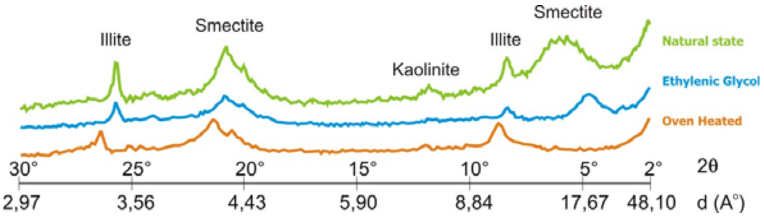

Figure 2. X-ray diffraction diagram for bentonitic material.

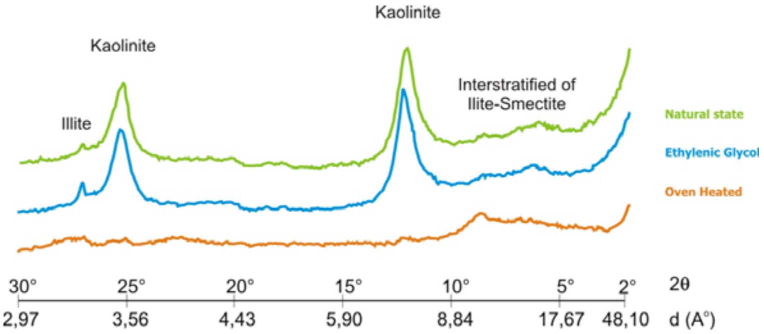

Figure 3. X-ray diffraction diagram for organic horizon.

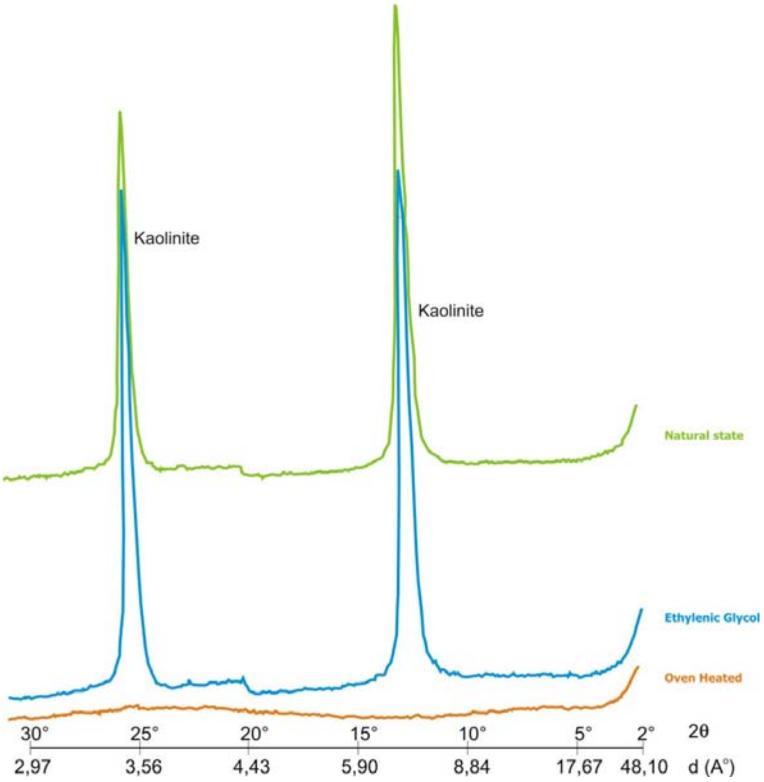

Figura 4. X-ray diffraction diagram for kaolinite pattern.

Batch Tests

Sorption was determined experimentally in batch tests, by measuring how much of a solute could be adsorbed by soil. A known volume of solution (Vw), containing an initial concentration (C_0) of a contaminant was placed into a container. A known mass of soil (M_s) was then added and the mixture was shaken and allowed to equilibrate. After equilibration, the soil was separated from the solution by centrifuging, and an aliquot of the supernatant fluid was taken. The concentration of the contaminant in this aliquot (C) was measured by means of atomic absorption and the concentration of the soil was calculated by:

$$S = V_w (C_0 - C) / M_s$$

In theory, when an inorganic compound has dissolved in ground water, it will be transported away from the source area by ground water flow. The contaminant does not travel at the same velocity as the ground water but can be slowed by the interaction with the soil matrix. This interaction is described as an adsorption isotherm and is so named because they are measured for a constant temperature. Different types of adsorption isotherms are defined according to their general shape and mathematical representation. For a Langmuir isotherm, the concentrations on the soil increase with increasing ground-water concentrations until a maximum concentration on the soil is reached. The isotherm can be represented as follows:

$$S = \frac{S_{max} \quad K \cdot C}{(1+K \cdot C)}$$

where S (M/M) is the concentration on the soil, S_{max} (M/M) is the maximum concentration on the soil, K (L^3/M) is the Langmuir adsorption constant and C (M/L^3) is the concentrations of the ground water. A Freundlich isotherm is given by the equation:

$$S = K \cdot C^{\alpha}$$

where K is the Freundlich adsorption constant and α is a positive parameter. Finally, a Linear isotherm is a special case of the Freundlich isotherm where the parameter α is equal to unity. In both models there is no maximum in adsorption sites.

Batch tests can also be used to assess retardation factors (R). The retardation factor can be interpreted in slightly different but equally valid ways, due its use. It can be the ratio of the ground water velocity (v) to the solute velocity (v_s), or the ratio of the time for the solute to travel from a source to an observation point divided by the time for the ground water to travel to the same path. And also can be considered to represent the number of pore volumes that must be flushed through a soil to remove the contaminant. All these definitions assume that the only process occurring is linear sorption which is usually defined as:

$$R = 1 + \frac{\rho}{\eta} Kd$$

where K_d is the partition coefficient (the ratio of the change in concentration of the contaminant on the soil to the change in concentration of the contaminant in the ground water), ρ (L^3/M) is the dry unit mass and is the porosity of the soil.

The equilibrium time for cadmium solutions must have been determined prior to their use in batch tests. This was done by continuously mixing the sub samples of soil with contaminant solution (2000 ppm. of cadmium) and taking aliquots at regular time intervals. These were then centrifuged and analysed by means of atomic absorption. The data showed no significant variations of metal concentration after 24 hours with both blocks of sample. This time was therefore adopted for all subsequent analysis. After establishing the time required to reach equilibrium, batch tests were carried out with 2000, 1500, 1000 and 500 ppm cadmium solutions. The data were analyzed by means of atomic absorption and the sorption isotherms plotted based on models of Langmuir and Freundlich. In accordance with the correlation coefficients, the model that best fitted the analysed data was chosen. After this procedure, the retardation factors were determined.

RESULTS

The isotherms obtained experimentally were strongly non linear and the sorption behaviour is illustrated in Figures 5 and 6 for each block of samples. The results confirm the influence of organic matter content and bentonitic material in the sorption of the studied metal. For both of the sample blocks assessed a similar preferential sequence of adsorption can be seen represented by the relative position of the isotherms curves with different percentages of soils. For sub sample 5 (composed exclusively of bentonitic material and organic horizon) the amount of sorption was greatest and decreased in the sub samples that contained a lower percentage of organic horizon.

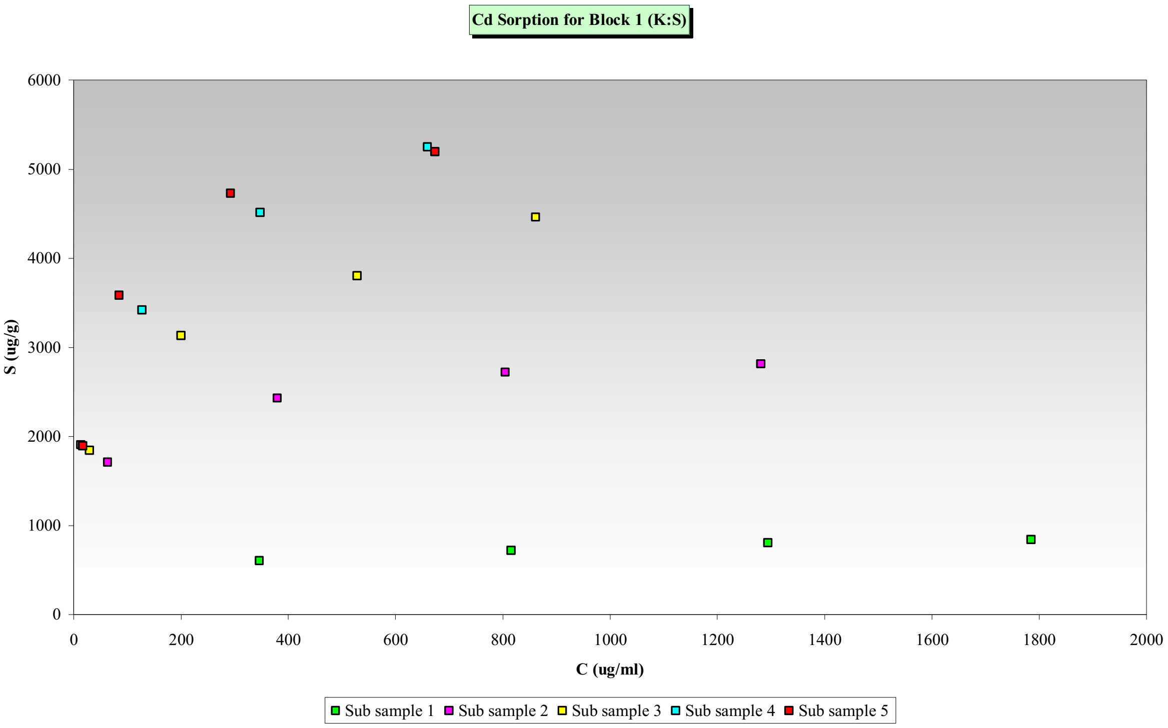

Figure 1. Cd sorption isotherms for block 1 (constituted basically by kaolinite and bentonitic material).

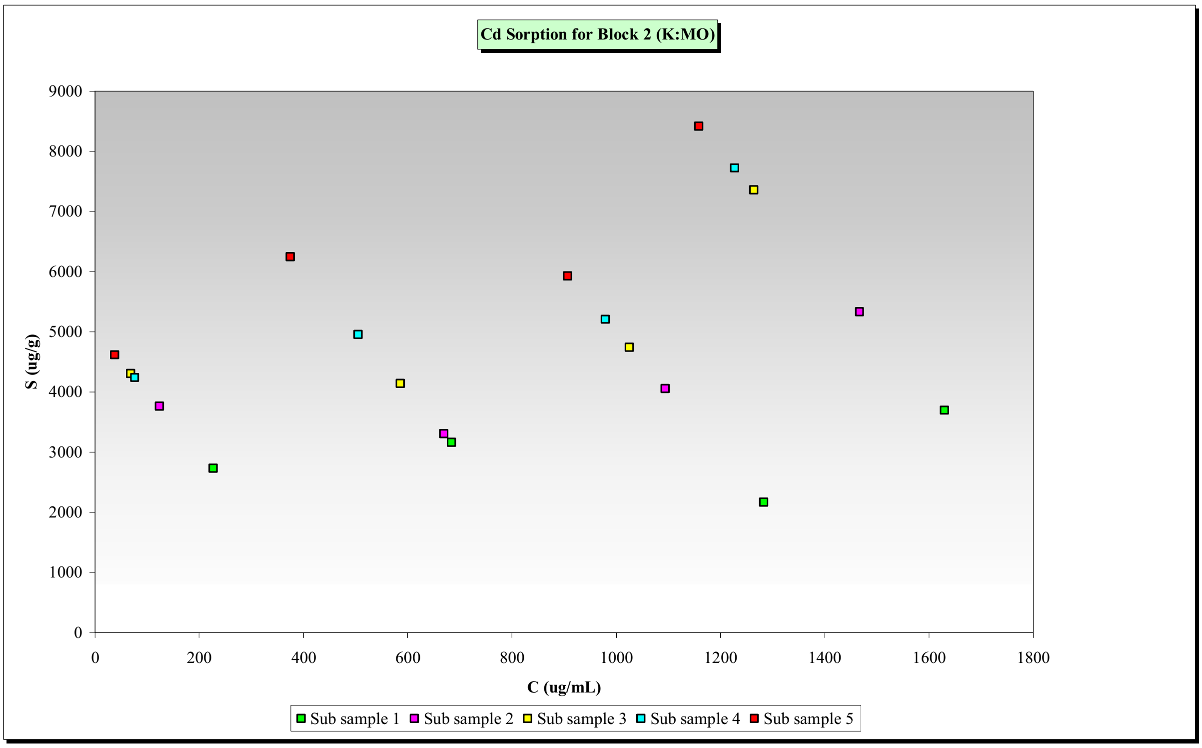

Figure 2. Cd sorption isotherms for block 2 (constituted by a mix of kaolinite pattern and organic superficial horizon).

Both blocks indicated that the Langmuir model was most appropriate, based on the high coefficient of determination (see Table 3). Its sorption behaviour is illustrated in Figures 7 and 8.

Table 3. Coefficient of determination of the isotherm models for cadmium.

	1st Block (K:S)		2nd Block (K:OM)	
Soil Mix	Freundlich	Langmuir	Freundlich	Langmuir
Sub sample 1	0,997	0,999	0,026	0,763
Sub sample 2	0,986	0,999	0,259	0,883
Sub sample 3	0,996	0,989	0,307	0,801
Sub sample 4	1,000	0,990	0,605	0,862
Sub sample 5	0,952	0,999	0,722	0,913

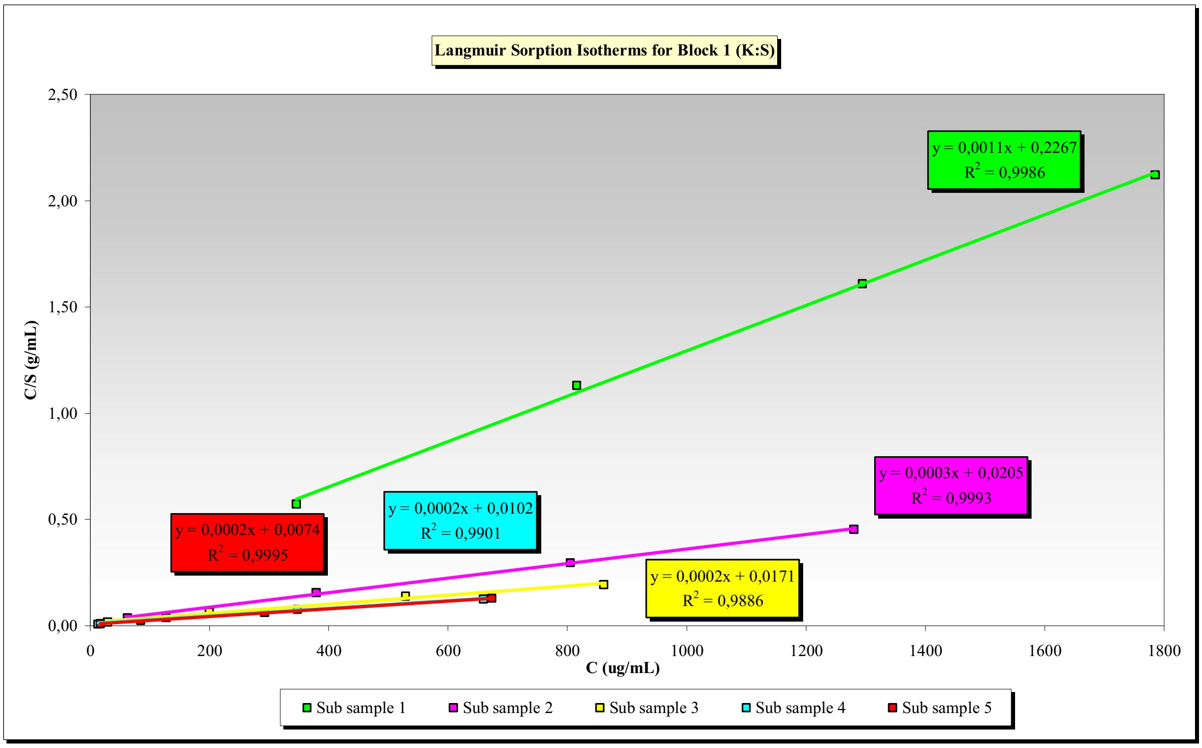

Figure 3. Langmuir isotherms for block 1 (constituted basically by kaolinite and bentonitic material).

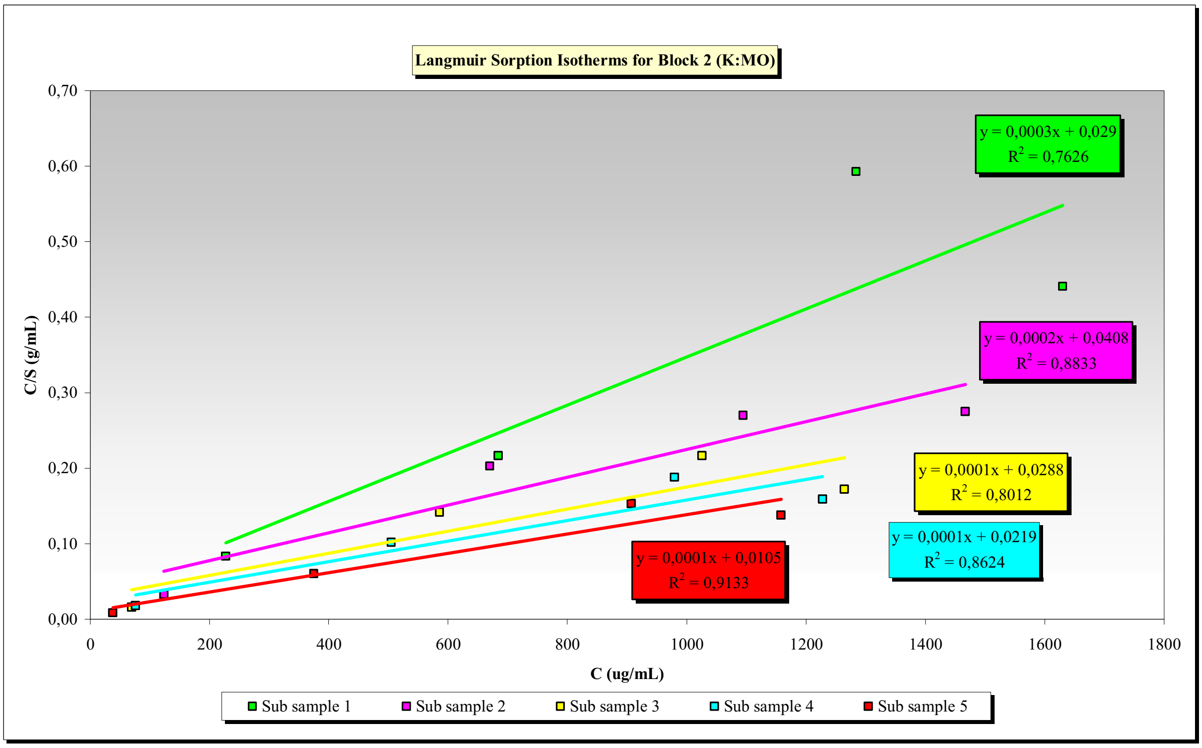

Figure 4. Langmuir isotherms for block 2 (constituted by a mix of kaolinite pattern and organic superficial horizon).

The soil property parameters used to achieve retardation factors are presented in Table 4 for block 1 and 2 respectively, where η is the soil porosity and ρ is the dry unit mass. The corresponding values of the sub samples 1 (kaolinitic soil or kaolinite pattern) and 5 (bentonitic material or organic horizon) were estimated from literature data (Kiehl, 1979). The intermediate values followed the same ratio presented before, in Table 1.

It is important to remember that the retardation factor depends on the flow velocity. This is important because the batch tests don't simulate the occurrence of flow through the ground.

Table 4. Retardation factors for cadmium. The higher values are marked in white.

		Block 1 (K:S)			**Block 2 (K:OM)**		
Soil Sample	**C0**	**η**	**ρ**	**R**	**η**	**ρ**	**R**
Sub sample 1	500 ppm	0,245	2,394	7,248	0,300	2,660	26,024
	1000 ppm			2,841			5,220
	1500 ppm			1,857			2,342
	2000 ppm			1,488			1,856
Sub sample 2	500 ppm	0,314	2,146	80,437	0,275	2,370	87,888
	1000 ppm			7,246			14,056
	1500 ppm			2,612			6,987
	2000 ppm			1,671			4,637
Sub sample 3	500 ppm	0,382	1,899	156,845	0,250	2,080	159,184
	1000 ppm			24,931			19,290
	1500 ppm			6,076			8,499
	2000 ppm			3,123			6,249
Sub sample 4	500 ppm	0,451	1,651	237,817	0,225	1,790	167,971
	1000 ppm			34,997			22,195
	1500 ppm			8,059			8,226
	2000 ppm			3,251			5,872
Sub sample 5	500 ppm	0,520	1,404	181,324	0,200	1,500	333,999
	1000 ppm			38,977			23,922
	1500 ppm			6,395			5,896
	2000 ppm			2,174			4,114

In general terms, it is possible to infer that the addition of the bentonitic material and organic horizon in blocks 1 and 2 was responsible for the gradual rise of the adsorption data, increasing its retardation factors and consequently, diminishing the mobility of the metal.

It can be seen in Table 4 that the retardation factors tend to reduce with the increase of the initial concentration of Cd which can be explained by the saturation of cadmium in clay minerals and organic matter.

Another fact that can be noticed is that sub samples 1 and 2 in block 2 present higher retardation factors than in block 1, probably because the mineralogy presented in the kaolinite pattern in block 2 is composed only of kaolinite, which has greater sorption than the illite and goethite found in block 1. In general, this behaviour is repeated in sub sample 3. Sub samples 4 and 5 show similar behaviour between both blocks.

CONCLUSIONS

Bentonitic material and organic matter have an important influence on the retention in soils of cadmium contamination. As expected, the greatest sorption occurred on sub samples 5, composed of 100% bentonitic material in block 1 and 100% organic horizon in block 2.

This effect can also be seen by the relative position of the isotherms for the different sample blocks. These show that the sorption is greatest for sub samples 5 (composed exclusively of bentonitic material and organic matter), decreasing in the sub samples containing a lower percentage of these materials.

In both blocks the Langmuir model was shown to best represent the data.

The retardation factors trend to decrease with the increase of the initial concentration of Cd due to the saturation of cadmium in clay minerals and organic matter.

In general, the greater retardation factors occurred in block 2, which was composed of kaolinite pattern and organic horizon material.

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