SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
ISSN 0104-5431

VOLUME ELEVEN, NUMBER TWELVE DECEMBER 2003

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SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
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FINAL DESTINATION OF CADMIUM FOUND IN CONTAMINATED SEWAGE SLUDGE IN MAIZE-CULTIVATED RED NITOSOIL

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ABSTRACT. *Remains of human activity, such as sewage sludge, caused by population growth, are a challenge to the environment and need urgent solutions. Cadmium from contaminated biosolid (sewage sludge) in Red Nitosoil, in PVC tubes (10 cm diameter and 80 cm height) located in greenhouse, has been analyzed. Natural biosolid in one treatment (control), cadmium-contaminated biosolid in two treatments (2,500 and 5,000 $\mu g\ g^{-1}$); cadmium- and lead-contaminated biosolid in other two treatments (2,500 Cd + 2,500 Pb and 5,000 Pb $\mu g\ g^{-1}$ respectively) were added to the 0 – 20 cm soil surface layer. Maize was the test plant in the triple replication experiment. The aerial part of maize plants, samples of surface soil (0 – 20 cm) and that within the tubes, divided into internal and external samples of each tube, were harvested seventy-five days after sowing. After the preparation and nitropercloric digestion of samples, Cd concentrations were measured by atomic absorption spectrometry. Cd concentrations in maize were within phytotoxic tolerance. There was no significant difference among treatments in the production of plant dry matter. Highest Cd concentration was found in the 0-20 cm soil layer and differed significantly from the rest.*

Key words: heavy metal; percolation; organic residues; pollution; cadmium.

RESUMO: *Os resíduos da atividade antróprica em sociedade, como o lodo de esgoto, são desafios ambientais do crescimento demográfico que necessitam soluções. Com este objetivo foi estudado o destino do cádmio do lodo de esgoto (biossólido) contaminado em Nitossolo Vermelho, em casa de vegetação, em tubos de PVC (10 cm de diâmetro e 80 cm de altura). À camada superficial de 0 a 20 cm foi incorporado: o biossólido natural num tratamento (testemunha); biossólido contaminado com cádmio em dois tratamentos (2.500 e 5.000 $\mu g\ g^{-1}$); e contaminado com cádmio mais chumbo em outros dois tratamentos (2.500 Cd + 2.500 Pb e 5.000 Cd + 5.000 Pb $\mu g\ g^{-1}$, respectivamente). No experimento com três repetições foi usado o milho como planta teste. Após 75 dias da semeadura coletaram-se: a parte aérea das plantas de milho, as amostras de solo da superfície (0-20 cm) e dos tubos-sonda que foram divididas em amostra interna e amostra externa de cada tubo-sonda. Após a preparação e digestão nitro-perclórica das amostras, as leituras das concentrações de Cd foram feitas pelo método de espectrometria de absorção atômica. As concentrações de Cd nas plantas de milho apresentaram-se dentro dos limites fitotóxicos. Na produção de massa seca das plantas não houve diferença significativa entre os tratamentos. No solo, a maior concentração de Cd foi encontrada na camada de 0-20 cm, que, diferenciou-se significativamente das demais.*

INTRODUCTION

Mankind learned by experience that soil produced less and less when continually cultivated. Consequently humans started to adopt certain agricultural practices, currently still in use, such as manuring, liming, crop rotation and others[1]. The addition of fertilizers to soil provides important nutrients to plants, namely, nitrogen (N), phosphorus (P) and potassium (K) which may be in default in the soil[2].

Population growth and the subsequent appearance of urban centers provided the dumping of human residues produced by development. Needless to say, this gives rise to environmental pollution that affects the general biota and man himself[3, 4]. Urban sewage[5], whose treatment causes sewage sludge[6], also known as biosolid, is of special importance. Through their penetration into the soil its components form a chain in the cycle and influence all forms of life. Pollutants, known as heavy metals[7], are among their components. Cadmium, the heavy metal currently under analysis, has been added to the environment in significant quantities with residues of mining, foundries, industrial refuse, sewage sludge and others[8]. On the other hand, studies are extant on the possibility of using sewage sludge in agriculture as organic manure even though it may have been contaminated by heavy metals [9, 10, 11].

Cd is naturally encountered in the soil as the product of rock meteorism whereby it is released. Under heavy oxidization cadmium oxidized mineral forms are CdO and $CdCO_3$[12] and its most important valence in the natural environment is 2+.

In soil solution Cd^{2+} is rapidly divided among the mineral, organic and solution phases. In fact, Cd^{2+}, and probably other metallic ions such as Zn^{2+}, is associated with water and forms a hydration complex. Ion Cd^{2+} is Lewis's strong acid and, associated with humidity, may cause the dissociation of protons. Cd may also exist in soil solution as a complex ion associated with other ligands. In soil solution the most important compounds are Cl^-, SO_4^{2-}, HCO_3^-, or organic links. Cd may also combine itself with ammonia ions in the form of $[Cd(NH_3)]^{2+}_{(aq)}$ or $[Cd(NH_3)_2]^{2+}_{(aq)}$ [13].

Brams and Anthony[14] analyzed cadmium absorption by wheat during a six-year period after addition of $CdCl_2$, concentration 7.5 kg ha^{-1}, to the soil. They noticed that concentration of cadmium greatly decreased in time. Data also indicated that 80% of Cd added was never recovered and failed to be detected up to 75 cm deep. The authors suggested that Cd was lost at the soil surface or at the soil sub-surface through the movement of soil particles.

Using doses 0, 20 and 40 t ha^{-1} of sludge complemented with 60, 80 and 100 kg ha^{-1} of N, P and K respectively, Silva (1995)[15] observed a linear increase in sugar cane production during the first year and did not detect any traces of heavy metals in the sugarcane broth.

Studies on the use of biosolids in soil for a variety of purposes [9, 10] are extant. There is, however, no agreement on the adequate dose for each culture, for each type of soil, for each type of climate, etc. This is perhaps due to difficulties in foreseeing the behavior of metals in different soil types and the nutrition requirements of each culture.

The current study analyzes the behavior of cadmium in contaminated sewage sludge applied to Red Nitosoil and its influence on maize culture.

MATERIALS AND METHODS

Soil

Red Nitosoil soil was collected in the region of the city of Maringá, PR, Brazil. Sampling occurred at depths 0 – 20, 20 – 40, 40 – 60 and 60 – 80 cm. Samples were placed separately in packages, taken to greenhouse and used in the experiment according to the exact positions in which they had been removed from the soil.

Table 1 shows chemical results of the soil's surface layer or arable section used (0 - 20 cm deep) prior to any treatment.

Table 1. Chemical characteristics of Red Nitosoil, 0-20 cm deep layer, used in experiment.

Soil	Cd(†)	Pb(†)	Fe(†)	Cu(†)	Mn(†)	Argila(‡)	silt(‡)	sand(‡)
	←		μg g^{-1}		→	←	%	→
RN(*)	4.50	39.2	119	25.9	448	52.0	27.0	21.0

(*) RN Red Nitosoil; (†) determination by atomic absorption spectrometry after nitric-perchloric digestion; (‡) Folk's granulometric classification[43] and calculation with method suggested by Suguio[44].

Table 2 shows characteristics of soil fertility of Red Nitosoil soil, layer 0 –20 cm depth, used in the experiment.

Table 2. Fertility of Red Nitosoil by chemical analysis (*).

Soil	pH		Al^{3+}	H^{+}+Al^{3+}	Ca^{2+}	Mg^{2+}	K^{+}	P	C	CTC
	(H_2O)	($CaCl_2$)	←		$cmol_c$ dm^{-3}		→	(μg g^{-1})	(%)	
TR	5.90	5.10	0.00	4.96	6.20	1.82	0.53	3.0	2.24	13.51

(*) Techniques: 1) pH in $CaCl_2$ 0,010 mol L^{-1} and pH in H_2O 1:2,5; 2) extractor Mehlich for K and P; 3) extractor KCl 1 mol L^{-1} for Ca^{2+}, Mg^{2+} and Al^{3+}; 4) [H^{+} +Al^{3+}] method of SMP.

Sewage sludge, its properties and preparation

The Paraná Water Company (SANEPAR), Maringá sector, provided the sewage sludge which was collected at the Maringá Sewage Treatment Plant (ETE-2). The sludge was dried, ground and homogenized before analysis. After nitric-perchloric digestion of the samples, concentrations of K, Ca, Mg, Cu, Zn, Fe, Mn, Pb and Cd were obtained by atomic absorption spectrometry[16]. Whereas N concentration was evaluated by Kjeldahl method[17], P was determined by UV-Vis spectrophotometry of the phosphorus-molybdenum complex[18]. Determination of C occurred by oxidation of organic matter by $K_2Cr_2O_7$ in excess and in a concentrated sulfuric acid medium and posterior excess titration of potassium dichromate[19]. Table 3 shows mean values obtained from analyses in triple.

Humidity and liming (dry) of sewage sludge were undertaken immediately on reception, pH was corrected to approximately 6.0 by a mixture of calcium carbonate and magnesium carbonate in the proportion of 3:1. Quantity of lime added was determined by calibration curve[20].

Table 3. Chemical characteristics of original sewage slime (without chemical treatment) in experiment.

Material	N	P	K	Ca	Mg	S	C	Cu	Zn	Fe	Mn	Pb	Cd
	%							$\mu g\ g^{-1}$					
Lodo(*)	2.92	0.82	0.18	3.08	1.02	0.32	24.3	146	1327	6128	262	122	3.50

(*) sewage sludge (biosolid).

Further, part of the sewage sludge was kept in its natural state, without any contamination, for control treatment; another part was contaminated by Cd (using $CdCl_2$) in $\mu g\ g^{-1}$, in 2,500 and 5,000 concentrations; still another part was contaminated by a mix of cadmium and lead, in $\mu g\ g^{-1}$, in 2,500 (Cd) + 2,500 (Pb) and 5,000 (Cd) + 5,000 (Pb) concentrations respectively. Lead was added as a possible interference factor in the behavior and final destination of cadmium in the system. Consequently sewage sludge was prepared for its incorporation to the arable soil layer (0 – 20 cm).

PVC (polyvinyl chloride) tube

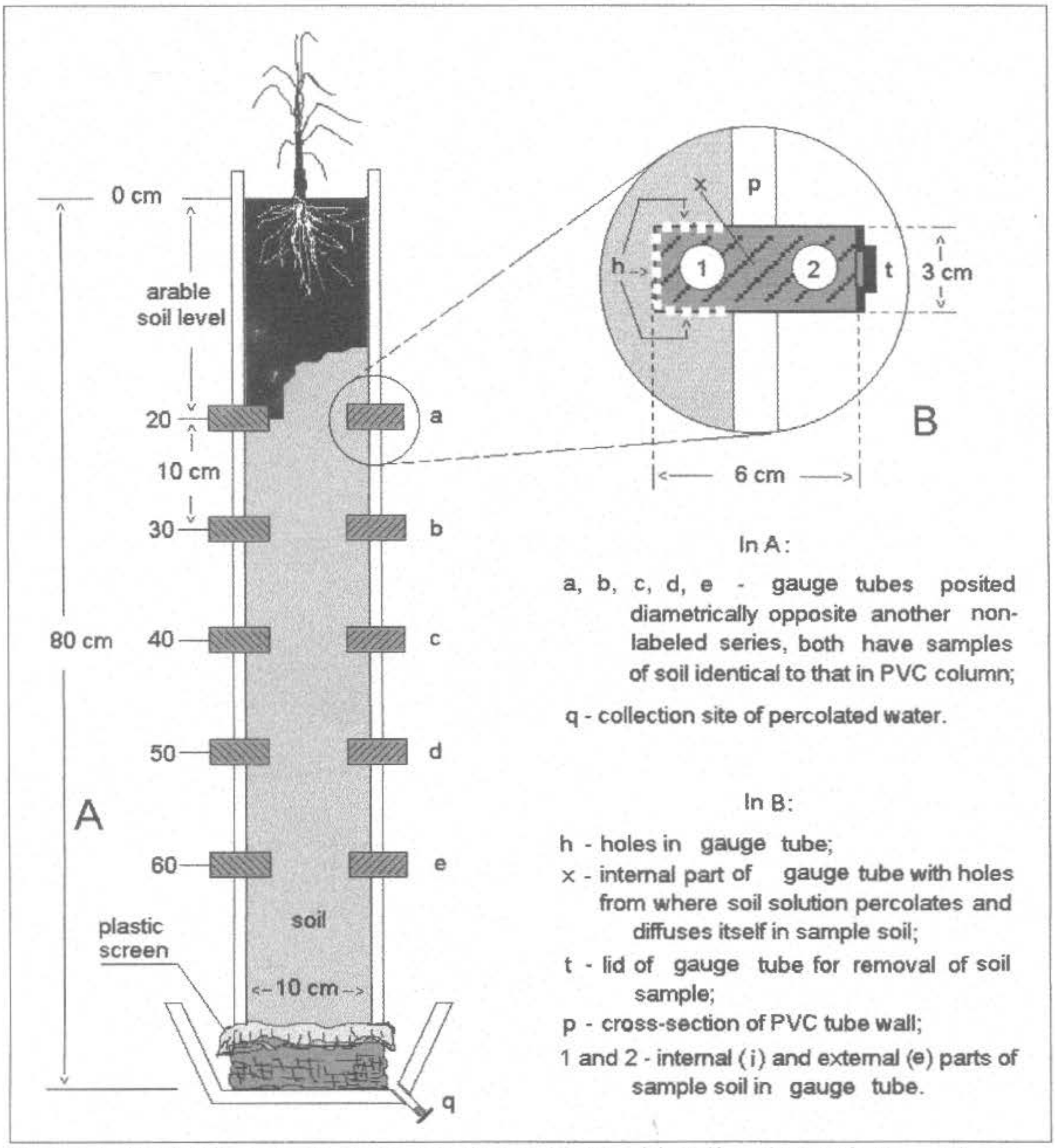
Figure 1 shows PVC tubes (10 cm diameter and 80 cm high) for used the experiment. Two series of gauge tubes were placed laterally, perpendicularly and diametrically opposite in the PVC tubes, at 10 cm depth, starting from 20 cm off the surface, as shown in Figure 1 – Part A. Gauge tubes collected soil samples at several depths without any damage to PVC tube or displacement of the soil column in the tube. Malleable plastic gauge tubes were fixed under pressure so that half remained in the interior of the PVC tube and the other half outside, with lid, as shown in Figure 1 – Part B. The inner side of the gauge tube was completely perforated with small holes so that soil solution could penetrate the gauge tube, or rather, percolate and diffuse itself throughout the soil and throughout that in the external part, as shown in Figure 1 – Part B. The existence of percolation and diffusion of the heavy metal cadmium could be verified at this sector.

Building, implantation and conduction of experiment

Three PVC tubes with gauge tubes were first prepared (Figure 1); they formed three replications for each type of sludge contamination. A total of 3 x (4 contaminations) + 3 x (1 control) = 15 PVC tubes was used.

A plastic screen was tied at the base and on the outside of each PVC tube to hold the soil in place and release the soil solution. Soil corresponding to the 60 – 80 cm layer was placed in each PVC tube together with the gauge tubes (e) filled with the same soil (Figure 1 – Part A). Identical process was used for the 40 – 60 layer soil with the respective gauge tubes (d, c) and for the 20 – 40 cm layer soil with the respective gauge tubes (b, a).

Sewage sludge contaminated with a 6 t ha^{-1} was added prior to placing the 0 – 20 layer soil in the PVC tubes, for each of the four types of contaminations above. This amounted to the following: 3 tubes with control (manured soil without pollutant); 3 tubes with contaminated soil containing Cd 2,500 $\mu g\ g^{-1}$; 3 tubes with contaminated soil containing mixture of Cd 2,500 $mg\ g^{-1}$ + Pb 2,500 $\mu g\ g^{-1}$; 3 tubes with contaminated soil containing a mixture of Cd 5,000 $\mu g\ g^{-1}$ + Pb 5,000 $\mu g\ g^{-1}$.



In A:

a, b, c, d, e - gauge tubes posited diametrically opposite another non-labeled series, both have samples of soil identical to that in PVC column;

q - collection site of percolated water.

In B:

h - holes in gauge tube;

x - internal part of gauge tube with holes from where soil solution percolates and diffuses itself in sample soil;

t - lid of gauge tube for removal of soil sample;

p - cross-section of PVC tube wall;

1 and 2 - internal (i) and external (e) parts of sample soil in gauge tube.

Figure 1. PVC tube (10 cm diameter; 80 cm high) with soil and test plant - maize: A – frontal vertical cut shows different soil layers and gauge tubes (**a**, **b**, **c**, **d**, **e**); B – amplification of frontal cut of gauge tube showing holes through which soil solution may percolate and diffuse itself through sampled soil in the internal (1) and external (2) parts.

After introducing non-contaminated (control) and contaminated sewage sludge in the first soil layer of each tube, the mixture was incubated for approximately 15 days, with humidity of each tube at 70% of field capacity and a 6.0 pH or whereabouts.

At the end of preparations for the experiment, 5 seeds of maize BR 300 were sown per vase. Pruning occurred with two plants per vase.

Tubes with maize plants were kept in a greenhouse. Plants were watered daily and position changes of tubes were done weekly at random. Watering occurred every seven days and double the amount of highest rainfall in the last 25 years in the region of Maringá (151.5mm) [21] was provided to percolate contaminant cadmium. Percolated solution was collected (Figure 1 – Part A), acidified at $pH<2$ with concentrated nitric acid and cadmium contents analyzed by atomic absorption spectrometry after pre-concentration by volume reduction in a water-bath.

Sample collection and analyses

Harvest of plants (aerial part) was done two and a half months after sowing, all at the same time; plants were washed and dried naturally and separately according to their distribution in vases. They were then placed in a buffer at 80°C for 48 hours[22]; weighted (Table 4) and ground in a Marconi MA 048 grinding machine. Plant samples (each formed by a set of plants) for analysis totaled 15.

A week after harvest soil samples from the 0 – 20 cm layer and from the gauge tubes were removed. The latter were divided into two parts, or rather, the internal part (i), corresponding to soil of the gauge tube placed within the PVC tube, and the external part (e) in which possible diffusion of the pollutant was analyzed. This totaled 150 soil samples of gauge tubes and 15 corresponding to the 0 – 20 cm layer.

Soil and plant samples, ground and dried at constant mass, were then decomposed by nitrate perchloride digestion.

Cadmium concentrations of the respective samples in duplicates were obtained by atomic absorption spectrometry, flame mode, according to handbook calibration rules and instructions by Welz & Sperling[23]. Atomic absorption spectrometer CG model AA 7000 ABC was used, with detection limit[23, 24] of 0.030 $\mu g\ mL^{-1}$. Tables 4 and 5 show the experimental results obtained.

Statistics

Experimental data was treated by variance analysis with Tukey test at 1% for mean comparison and SANEST was the software employed for statistical analysis.

RESULTS AND DISCUSSION

Rates 2,500 and 5,000 $\mu g\ g^{-1}$ of pollutant were randomly chosen due to the fact that they represent highly contaminated sludge that would be applied to soils and in 6 t ha^{-1} doses. If nothing occurs with the heavy metal in percolation and exportation by plants when applied to sludge in a certain soil, the biosolids may be applied to the soil without any further concern. Such an inference may be done, since cadmium, in the form in which it has been added, is available in soil solution without any previous mineralization of the sludge's organic matter.

Although lead is found naturally on the earth crust at mean values of 12.5 mg kg^{-1} [25] and 16 mg kg^{-1} [26, 27], it has been constant from the very beginning of human civilization[28]. In 1981 lead was the fifth element in world metal production ranking, following Fe, Cu, Al and Zn[29]. At present it is ubiquitous in the environment [30-35]. Since it is also found in sewage sludge, it has been added so that possible interferences in Cd behavior could be studied.

Table 4. Production of dry matter from plant's aerial part and cadmium concentration.

Treatments	Production in g (*)	Cd concentration in µg g^{-1}(†)
Control	4.22 a (‡)	0.80 b (‡)
Cd (2,500)	3.79 a (‡)	7.10 a (‡)
Cd (5,000)	3.52 a (‡)	6.71 a(‡)
Cd (2,500) e Pb (2,500)	3.82 a (‡)	6.70 a(‡)
Cd (5.000) e Pb (5,000)	3.35 a (‡)	9.20 a(‡)

(*) mean values of the experiment's three replications; (†) mean values of two analytic replications; (‡) means followed by different letters differ at 1% level of significance.

Table 5. Mean of Cd concentration (µg g^{-1}) in Red Nitosoil for triplicates of different treatments.

Depth (cm)		Treatments				
		Control	Cd (2,500)	Cd (5,000)	(Cd + Pb) 2,500(†)	(Cd + Pb) 5,000(‡)
Surface		4.94 a*	21.77 a*	31.88 a*	20.82 a*	32.31 a*
20	**i**	4.88 a*	4.86 b*	4.94 b*	4.89 b*	4.85 b*
	e	4.87 a	4.86 b	4.92 b	4.88 b	4.83 b
30	**i**	4.87 a	4.85 b	4.92 b	4.86 b	4.83 b
	e	4.86 a	4.85 b	4.89 b	4.86 b	4.82 b
40	**i**	4.86 a	4.85 b	4.88 b	4.83 b	4.80 b
	e	4.83 a	4.83 b	4.86 b	4.83 b	4.79 b
50	**i**	4.82 a	4.83 b	4.86 b	4.80 b	4.79 b
	e	4.80 a	4.82 b	4.86 b	4.77 b	4.77 b
60	**i**	4.73 a	4.80 b	4.83 b	4.76 b	4.77 b
	e	4.68 a	4.77 b	4.82 b	4.74 b	4.76 b

i – internal part of gauge tube; **e** – external part of gauge tube; (†) contamination of biosolid in treatment, in µg g^{-1}, for each element; (‡) contamination of biosolid in treatment, in µg g^{-1}, for each element; * means followed by different letters differ at 1% significant level.

Maize plants

Maize plants were harvested 75 days after germination since they exhibited certain deficiencies: leaves began to turn purple, probably due to P deficiency; later, they manifested yellowing symptoms (chlorosis), probably due to N deficiency, according to Kabata-Pendias & Pendias[36]. Table 4 shows the dry part of the aerial part of the plant. Variance analysis failed to show any significant difference in dry matter production.

Cd concentration in the aerial part of plant (Table 4) shows that Red Nitosoil soil had similar values, including treatments in which Pb has been employed as interference factor. It differed, however, from the control in which the least absorption by plant occurred owing to less availability or to low concentration.

Lake (1987)[37] states that absorption of Cd applied with sewage sludge immediately before planting is at least 10 times higher than that when sowing is done in sludge-treated soils during consecutive years.

According to Kabata-Pendias & Pendias (1992) [36], cadmium may have the following concentration rates in the dry tissues of mature leaves for different species: a) normal or sufficient concentration, from 0.05 to 0.2 $\mu g\ g^{-1}$; b) excessive or toxic, from 5 to 30 $\mu g \cdot g^{-1}$; c) tolerated in agronomic species, 2 $\mu g\ g^{-1}$. Experimentally obtained rates are found within the phytotoxic range (Table 4). Cadmium concentration in the control was lower than that tolerable, albeit above normal.

Cadmium in the soil

Results of Red Nitosoil soil treated with either contaminated or non-contaminated sewage sludge (Table 5) showed an accumulation of heavy metal at the surface (0 – 20 cm depth level) where contaminated sewage sludge was applied in all treatments. Heavy metals generally fix themselves at 0 – 20 cm depth layer, precisely the layer with the highest fertility index and, obviously, greatly used in agriculture[38].

Analyzing interactions between humus acids and heavy metals, Ladonin and Margolina (1997)[39] present a hypothesis for heavy metal retention. They admit a chemical fixation between the active sites of humus acids and metals.

Such a "fixation", or rather, a chemical link, occurs by the formation of external or internal layer complexes[40]. Interactions between cadmium cation and the simple or homologue composite ligand within the external layer are electrostatic according to [1]:

$$\mathrm{Cd_{aq}}^{(2+)} + \mathrm{L_{aq}} \rightleftarrows \{[\underbrace{\mathrm{Cd_{aq}}^{(2+)} \ldots \mathrm{L_{aq}}^{(n-)}}_{\downarrow \atop \text{electrostatic interaction}}]^{[(n-)+(2+)]}\}_{aq} \qquad [1]$$

where L is the ligand which may be either a simple composite (Cl^{-}, $CO3^{2-}$, $PO4^{3-}$, amino-acids etc) or a homologous composite (fulvic and humic acids, proteins, metallic oxides and hydroxides etc).

In the internal layer complexes the interaction between cadmium and the ligand is covalent [2]:

$$\mathrm{Cd_{aq}}^{(2+)} + \mathrm{L_{aq}}^{(n-)} \rightleftarrows \{\underbrace{[M - L]}_{\downarrow \atop \text{covalent interaction}}{}^{(n-)+(2+)]}\}_{aq} + x.H_2O \qquad [2]$$

In all treatments Cd concentrations comprising horizontal direction, external and internal parts of the gauge tubes, and vertical direction, 20 – 60 cm depth layer, did not have statistically significant differences. They were compatible with control and thus confirm that neither lixiviation nor diffusion of heavy metals occurred in these directions. A similar study with cadmium in Dark Red Latosol showed the same conclusion[41].

Although clay makes up 52% of soil (Table 1), its cationic change capacity amounts to 13.51smol$_c$ dm^3 (Table 2). This is rather low when compared to certain types of clay and shows slightly expansive clay[7].

Studies on metal movements in soils treated with organic residues suggest that less than 1% of metals may be lixiviated. These metals may either be adsorbed or made more complex, till changes occur in the system[42]. This fact has been detected in current experiment since cadmium was not found in percolation water in the soil of the PVC column when irrigation, imitating torrential rain, was executed weekly.

When data in Tables 4 and 5 are analyzed with regard to treatments for possible Pb interference in Cd, it has been observed that the former failed to change Cd behavior in any treatment.

CONCLUSIONS

The experimental results led to the following conclusions:

The heavy metal Cd in soil was retained at the arable soil level (0 – 20 cm depth) in all treatments.

No significant difference occurred in the production of dry matter from the aerial part of plants.

When Cd absorption by the aerial part of maize plants is taken into account, Cd concentration rate maintained itself at the starting level of phytotoxic concentrations.

Lixiviation and metal diffusion have not been observed in layers below the arable level.

Pb interference with Cd behavior has not been detected in any soil or plant parameter.

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A STUDY OF THE CORROSION INHIBITION OF CARBON STEEL IN AMMONIACAL MEDIA DILUTED BY N-CYCLOHEXYL BENZOTHIAZOLE SULPHEN AMIDE

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ABSTRACT

The inhibition effect of N-cyclohexyl benzothiazole sulphen amide (NCBSA) was studied on the corrosion of carbon steel in diluted ammoniacal solution at temperatures of 25 °C and 30°C.

The effects of the inhibitor on the corrosion were investigated and determined by using electrochemical measurements (curves of intensity - voltage). The efficiency of NCBSA increased with increase in concentration, but decreased with increase in temperature. Free energy of activation was determined from Arrhenius type equation. Experimental data fitted on adsorption isotherm of Langmuir type, while the results were correlated to the chemical structure of the inhibitor.

RESUMO

A inibição da corrosão do aço carbono por N-ciclohexil benzotiazol amida (NCBSA) em solução amoniacal diluída foi estudada á 25 e 30 °C. Os efeitos do inibidor foram estudados e determinados usando medidas eletroquímicas (curvas de intensidade-voltagem). A eficiência do inibidor (NCBSA) aumentou com a concentração e diminuiu com o aumento na temperatura. A energia de ativação foi determinada usando a equação de Arrhenius. Os resultados expereimentais seguem o isoterma de adsorção de Langmuir e foram relacionados com a estrutura do inibidor.

KEYWORDS: carbon steel, ammoniacal media, inhibitor, N-cyclohexyl benzothiazole sulphen amide

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INTRODUCTION

Before 1960, the treatment of the carbon steel corrosion in the systems of water cooling was based on inorganic inhibitors such as chromates, nitrates, polyphosphates and zinc salts.[1-3] The use of chromates is restricted because of their toxicity, while the nitrates are efficient in concentrations that economically disadvantageous, being also easily decomposed by bacteria.[3]

Particular attention has been given lately to the use of polyphosphates and their derivates.[4] The advantageous use of these compounds consists in the lack of toxicity. Moreover, only a concentration of a few ppm is necessary for the protection of great systems of water supply. Yet they can be media favourable for the development of microorganisms.

Ever since 1960 more advanced treatments based on organic compounds[5,6] have been proposed to improve protection against corrosion.

The efficiency of the corrosion inhibition by the organic compounds is closely related to the structure and the properties of the layer formed on the metal surface under experimental conditions. The process of the adsorption of the organic compounds is attributed to the effects of the functional groups grafted on aromatic nuclei.[7,8]

It appeared that the adsorption depended especially on the electronic structure of the molecule and that the inhibiting effect increased with the number of aromatic nuclei.

The organic compounds containing sulphur and nitrogen have been utilized for the corrosion inhibition of carbon steel in acid media, the results showing that the most inhibitors act through adsorption at the metal surface.[9-10] The power of adsorption and consequently the strength of the inhibiting effect are dependent on the nature of the organic compounds, on the nature of the metal and of corrosive medium.

The current investigation establish the role of NCBSA in improving the passive films resistance towards general corrosion of the carbon steel in diluted ammoniacal solution of 10^{-3} N concentration.

EXPERIMENTAL DETAILS

The sample chosen for investigation is carbon steel LC 35 having the following composition: C = 0.35%, Mn = 0.65%, Si = 0.25%, S = 0.035% and iron up to 100%. For all experiments the carbon steel samples were polished with sand paper, cleaned in water, degreased in ethilic alcohol and dried in warm air.

The corrosion medium was the ammoniacal solution of 10^{-3} N concentration in contact with air at a temperature of 25°C and 30°C.

The tested inhibitor was N-cyclohexyl benzthiazole sulphen amide (NCBSA) and the measurements were made for its concentrations of 10^{-4} M, 2×10^{-4} M, 3×10^{-4} M and 4×10^{-4} M.

The electrochemical measurements were made using a standard corrosion cell. The working electrode was a carbon steel plate with an area of 4 cm^2. A calomel-saturated electrode was used as a reference electrode and the auxiliary electrode was a platinum plate. Data were computerized.

RESULTS AND DISCUSSION

The polarization curves are presented in figure 1. As compared to the non-inhibited solution, the corrosion potential shifted towards positive values. The presence of NCBSA increases the anodic over-voltage and leads to a decrease in the corrosion current. Up to current densities of 5 mA dm^{-2} the anodic potentials present a slight increase towards higher positive values. At current densities higher than 5 mA dm^{-2} the increase in potentials is significant, which supposes the inhibitor desorption on electrode surface. The decrease in the corrosion current was associated with a significant shifting of the corrosion potential towards higher values. This suggests that when the inhibition is mixed type it is preponderently anodic. The Tafel segments in the curves of cathodic polarization have small slopes being in the vicinity of the cathodic current limit. The nature of this limit is probably determined by the total transfer of all the cathodic-reduced compounds such as: O_2, NH_4^+, H_3O^+. The retardation of the metal ionization by inhibitors is stronger than the stimulation of the cathodic process, the free corrosion potential of carbon steel significantly increasing with the increase in NCBSA concentration.

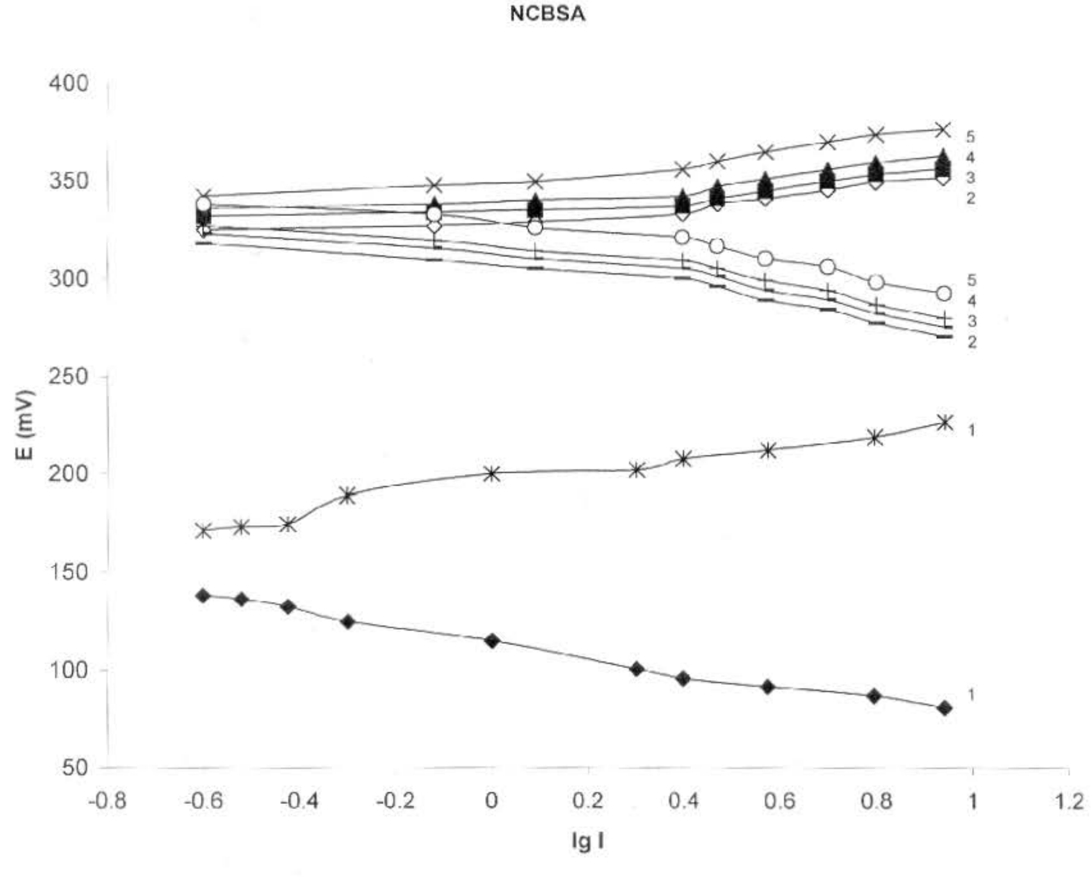

Figure 1. The polarization curves for carbon steel in ammoniacal solution 10^{-3} N in the presence of NCBSA at different concentrations: (1) 0.0; (2) 10^{-4} M; (3) 2×10^{-4} M; (4) 3×10^{-4} M; (5) 4×10^{-4} M.

In inhibitor solutions the steel remains active and behaves as an anode and dissolves after a Tafel-type slope b_a at 36±3 mV (figure 2)

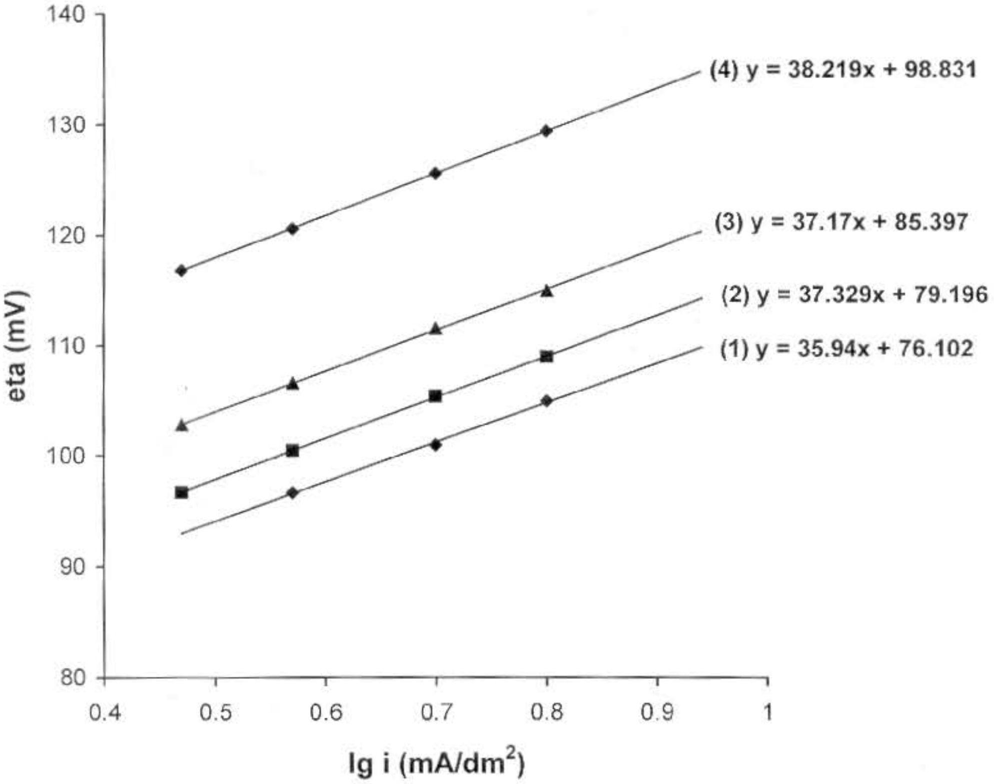

Figure 2. Graphical representation of $\eta = f(\lg I)$ for carbon steel in ammoniacal solution 10^{-3} M in the presence of NCBSA at different concentration: (1) 10^{-4} M; (2) 2×10^{-4} M; (3) 3×10^{-4} M; (4) 4×10^{-4} M.

The corrosion current can be calculated from Tafel-type equation with potentials far apart from the corrosion potential for a theoretical slope b_a equal to $2{,}3RT/zF\alpha$ mV, as follows:

$\lg I_{cor} = 2.06 - 0.026(\eta_2 - \eta_1)$ (1), for the temperature of 25°C;

$\lg I_{cor} = 2.12 - 0.025(\eta_2 - \eta_1)$ (2), for temperature of 30°C,

where:

I_{cor} = corrosion current in the presence of inhibitor;

η_1 = galvanostatic over-voltage for non-inhibiting solution;

η_2 = galvanostatic over-voltage for inhibiting solution.

The efficiency of inhibition represented by the rate was calculated from the formula:

$$P = \frac{i_{cor_1} - i_{cor_2}}{i_{cor_1}} \qquad (3)$$

where: i_{cor1} = corrosion current for non-inhibiting solution

i_{cor2} = corrosion current for inhibiting solution
The results are presented in Table:

Table 1. The electrochemical parameters for carbon steel in ammoniacal solutions 10^{-3} N in the presence or absence of NCSBA, the percent P obtained from the galvanostatic polarization η and the corrosion rate at 25°C and 30°C.

	25°C					30°C				
C_{NCBSA}	0	10^{-4}	$2x10^{-4}$	$3x10^{-4}$	$4x10^{-4}$	0	10^{-4}	$2x10^{-4}$	$3x10^{-4}$	$4x10^{-4}$
E_{cor} (mV)	159	267	272	278	284	153	260	265	270	277
I_A (mA dm^{-2})	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75	8.75
η (mV)	67	107	111.7	118.6	132	64	102.5	107.5	111.6	119
I_{cor} (μA dm^{-2})	116	10.5	7.9	5.3	2.3	132	14.5	10.8	8.5	5.9
P (%)	-	90.9	93.2	95.4	98	-	89	91.8	93.5	94.6
K_g (mg m^{-2} h^{-1})	8.1	0.74	0.56	0.37	0.16	9.3	1.02	0.76	0.6	0.42

The variation of the corrosion rate with an inhibitor concentration is presented in Figure 3. The corrosion rate decreases with the increase in the inhibitor concentration and increases with the increase in temperature, which indicates a stronger desorption of the inhibitor on the electrode surface. It is known from a previous work,[11] where the electrochemical measurements were associated with Mössbauer spectroscopy measurements, that in absence of the inhibitors the carbon steel surface is covered with a nonstoichiometric iron oxide layer.

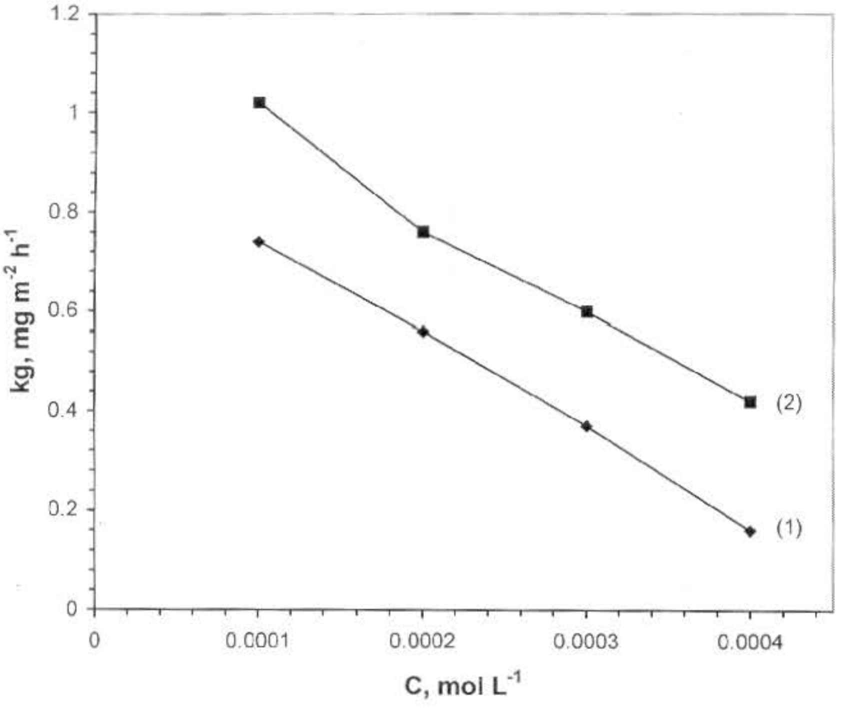

Figure 3. The variation of the corrosion rate with NCBSA concentration: (1) 25°C; (2) 30°C.

The investigation of the inhibition led to the conclusion that the experimental data fit an adsorption isotherm of Langmuir-type expressed by the relation:

$$\frac{\theta}{1-\theta} = Kc \qquad (4)$$

where: $\theta = P/100$
K = the equilibrium constant of the adsorption process;
c = the inhibitor concentration in the solution mass

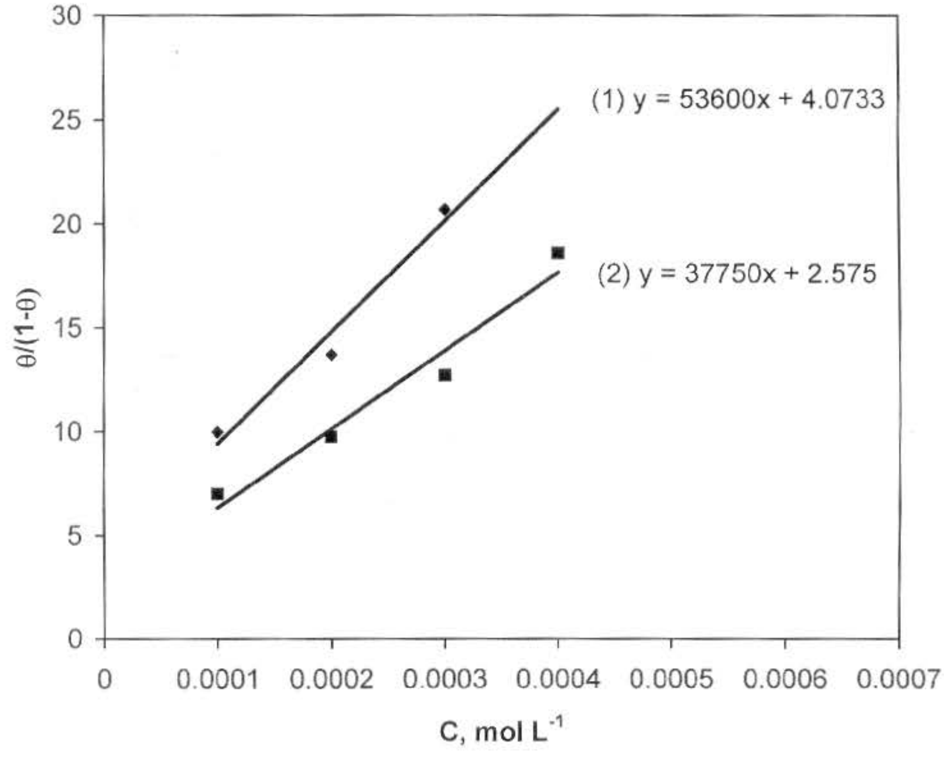

Figure 4. Langmuir-type diagram for corrosion inhibition of carbon steel in ammoniacal solution 10^{-3} N in presence of NCBSA at different temperatures: (1) 25°C; (2) 30°C.

Data are presented in Table 2. Figure 4 illustrates the results of a Langmuir-type diagram. The standard free energy of adsorption was calculated from the formula:

$$\Delta G_{ads}^{0} = -345.6 \cdot 10^{3} \lg \frac{K_1}{K_2} \qquad (5)$$

The values of K are relatively high indicating an electrostatic interaction between the double layer and the adsorbed molecules. The equilibrium constants of adsorption imply a more efficient adsorption at the temperature of 25°C than at 30°C. The values of ΔG_{ads}^{0} are negative, which shows the adsorption process takes place spontaneously. The activation energy characteristic to the corrosion inhibition was mathematically calculated from Arrhenius-type equation for tow different temperatures.

$$E_a = -345.6 \cdot 10^3 \lg \frac{k_{g_1}}{k_{g_2}} \quad (6)$$

Table 2. The activation energy, the equilibrium constant and the standard free energy of adsorption for the carbon steel sample in ammoniacal solution 10^{-3} N in presence of NCBSA.

C_{NCSBA} (mol L^{-1})	E_a (kJ mol^{-1})	25°C		30°C		ΔG_{ads}^0 (kJ/mol)
		θ/(1-θ)	K (mol^{-1})	θ/(1-θ)	K (mol^{-1})	
0	21.5	-	53.6 x 10^3	0	3.7 x 10^3	-52.81
10^{-4}	48.6	9.98		7		
2 x 10^{-4}	45.8	13.7		9.75		
3 x 10^{-4}	72.5	20.7		12.7		
4 x 10^{-4}	144.8	49		18.6		

The values of the activation energy depend on the nature and concentration of the inhibitor.

CONCLUSIONS

Concurrently with the increase in the current density the anodic potentials of the steel electrodes in ammoniacal solution 10^{-3} N containing NCBSA are shifted towards higher values, while the cathodic potentials are shifted towards lower values. The presence of NCBSA in the corrosion medium increases the anodic and cathodic over-voltage and decreases the corrosion current. These changes increase with the increase in NCBSA concentration.

The decrease in the corrosion current was associated to a significant shift of the corrosion potential towards higher values. This suggests that when the inhibition is of mixed-type it is predominantly anodic.

NCBSA behaves as an inhibitor of generalized corrosion. The efficiency of inhibition increases with the increase in the NCBSA concentration, but decreases with the temperature increase.

Inhibition was associated with the NCBSA adsorption on the steel surface. Due to its great efficiency, it appeared that a complex was formed between NCBSA and different metallic cations in steel composition. These complexes can form passivating layers that are stable at the steel surface, thus decreasing the corrosion rate. The adsorption of these inhibitors on the steel surface fits the conditions of Langmuir-type isotherm of adsorption.

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