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Adsorption of Heavy Metals on Bentonitic Soil for Use in Landfill Liners

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Hazardous heavy metal ions such as copper, zinc, nickel, chromium, cadmium, and lead engender a potential risk to human health. Among the processes involved in the retention of these contaminants, adsorption is advantageous for removing toxic metals because of its environmentally friendly aspect, efficiency, and low-cost operation. Information on the adsorption of heavy metals in soils from the semiarid region of northeastern Brazil is still scarce. In this study, the adsorption of heavy metals (Cd, Cu, Zn, Ni, and Pb) by a semiarid Brazilian bentonitic soil is investigated. This soil has been used as a bottom liner in an experimental municipal solid waste (MSW) cell located in Campina Grande, State of Paraíba, Brazil. The experimental cell consists of a landfill unit on an experimental scale, with the same constructive elements of a sanitary landfill. Disturbed and undisturbed samples of the investigated soil were collected at a quarry in the rural zone of Boa Vista (state of Paraiba, Northeast Brazil). Sorption attributes were determined via batch tests with a soil-solution ratio of 1 : 12.5 (4 g of dry soil to 50 mL of solution). Linear, Freundlich, and Langmuir isotherms were fitted to the experimental data, using as fitting parameters Pearson correlation coefficient (R^2) and p value with a significance level $\alpha = 5\%$. The ascending order of maximum adsorption capacity for heavy metals followed the series Ni < Cr < Zn < Cd < Cu < Pb. The maximum adsorbent capacities obtained were similar to those of other Brazilian soils and other adsorbents. Therefore, the studied soil has a high potential to be used in the retention of heavy metals.

1. Introduction

Inadequate disposal of residues from industrial sectors has caused considerable environmental impacts. These residues contain pollutants that can be organic and inorganic [1, 2], heavy metals being the major components of inorganic pollutants. Heavy metal sources can have natural origin, such as rock weathering and volcanic eruptions, and anthropogenic origin, including mining, agriculture, and industry [3–5]. Inappropriate waste management, particularly from anthro-

pogenic activities, can result in contamination of air, soil, and water by the release of heavy metals [6, 7].

Some of the hazardous heavy metal ions that potentially endanger human health are Cu, Zn, Ni, Cr, Cd, and Pb, which are not recyclable and accumulate in living organisms [8, 9]. Furthermore, reports indicate that the concentrations of heavy metal ions in water systems are alarmingly higher than the limits recommended by the World Health Organization (WHO) [10]. The toxicity and permissible limits of various metal ions are listed in Table 1.

TABLE 1: Heavy metal ions, corresponding adverse effects, and permissible limits according to WHO.

Heavy metal	Health Hazards	Permissible limit (mg/l)	References
Cd	Kidney damage, renal disorder, human carcinogen, and emphysema	0.003	Pyrzynska [11]
Pb	Brain damage, anemia, anorexia, vomiting, and diseases of the circulatory and nervous systems	0.050	Mahmoud et al. [12]
Cr	Headache, diarrhea, nausea, vomiting, carcinogenic effects, and lung tumor	0.050	Xu et al. [13]
Cu	Liver damage, Wilson's disease, and insomnia	2.500	Kumar et al. [14]
Zn	Depression, lethargy, neurological signs, dehydration, anemia, and increased thirst	5.000	Shobana et al. [15]
Ni	Dermatitis, nausea, chronic asthma, coughing, and lung cancer	2.000	Gupta and Kumar [14]

Mobility and potential toxicity of heavy metals in soil is determined by retention and release reactions with the soil matrix, which include precipitation, dissolution, ion exchange, and adsorption/desorption reactions via inner and outer sphere complexations [16]. Among these processes, adsorption has become advantageous for removing toxic metals because of its environmentally friendly aspect, efficiency, and low-cost operation.

Diverse adsorbents (e.g., active carbon, zeolite, chitosan, and clay) have been studied and developed to immobilize toxic heavy metals [17, 18]. A commonly used technique is the incorporation of sorbents (which have a high retention capacity for potentially toxic metals) into sandy soil, such as bentonite.

Bentonite is a 2:1-type layered aluminosilicate with a crystalline structure consisting of one alumina octahedral layer between two silica tetrahedral layers [19]. The primary clay mineral in bentonite is montmorillonite.

Results from soil adsorption studies indicate that adsorption depends on pH, concentration, contact time, and temperature [20, 21]. Most studies on the retention of heavy metals in soils are limited to soils from temperate climate regions [22]. In the past decades tropical soils have also been investigated [23]; however, related studies using soils of the Brazilian semiarid region are scarce [24–26]. Since the 1970s, this region has been affected by severe anthropic hazards; together with the substantial increase in solid waste generation, this has resulted in landscape transformation [27].

The soils of the semiarid region typically have a thin altered layer that covers the bedrock [28, 29], and exhibit mineral characteristics due to the stages of their formation or physical and chemical weathering [30, 31]. In addition, feldspars and ferromagnesian minerals rapidly decompose in semiarid regions, whereas the concentration of iron and aluminum oxides remains stable [32]. The sorption of heavy metals in soils from the Brazilian semiarid region was analyzed by researchers such as Chaves and Tit [33], Vasconcelos et al. [34], Meneguin et al. [35], Araujo et al. [36], and Barros et al. [37].

Bentonitic soils are commonly used in sanitary landfill liners because of their low water permeability; moreover, as indicated by Fletcher and Sposito [38] and Dixon et al. [39], the expansion of particles favors the adsorption of

metal cations in confined conditions, as a result of the complexation of metals in water present in interbasal or interlamellar spaces of clay minerals, which is known as inner-sphere complex.

In Brazil, the sorption of heavy metals in soils used in sanitary landfill liners was studied by Matos et al. [40], Fontes and Gomes [41], Azevedo et al. [42], Boscov [43], Fontes et al. [30] and Marques et al. [44]. However, these studies focused on soils from the Southeast region of Brazil. In the Brazilian semiarid region, Silva et al. [45] studied the adsorption of Ni in a soil employed in a sanitary landfill liner. Nonetheless, the leachate produced in sanitary landfills is a complex effluent with several heavy metals in its composition, as listed in Table 2.

In this study, the adsorption of heavy metals (Cd, Cu, Zn, Ni, and Pb) by a bentonitic soil from the Brazilian semiarid region is evaluated. This soil has been used as a bottom liner in an experimental municipal solid waste (MSW) cell located in Campina Grande, State of Paraíba, Brazil.

2. Materials and Methods

2.1. Study Area

2.1.1. Experimental Cell. The experimental MSW cell consists of a landfill unit on an experimental scale, and it has the same constructive elements present in a sanitary landfill. The built cell (Figure 1) has a cylindrical shape with a diameter of 2.0 m, height of 3.6 m, and volume of 11 m³.

The cell instrumentation enables the monitoring of parameters related to the biodegradable behavior of the MSW, such as total and layered vertical deformations and liquid levels. Moreover, the cell has gas and liquid drains and waste collection points. The liner of the experimental cell consisted of layers of compacted clayey soil with low permeability to water and collected from a quarry in the city of Boa Vista, Paraíba state.

The liner was designed considering the maximum dry bulk density and optimal moisture content for the Proctor normal compaction energy. The speed test was used to determine the hygroscopic soil moisture of in the field, and the amount of water required to achieve the optimal soil moisture was calculated. The liner consisted of a compacted

TABLE 2: Concentration ranges of heavy metals commonly found in sanitary landfill leachate.

Metal	Concentration range (mg/L)	Metal	Concentration range (mg/L)
Ar	0.005–1.600	Fe	0.08–5.50
Cd	0.00002–0.4	Al	0.01–1.4
Pb	0.0005–2.0000	Hg	0.00005–0.50
Cu	0.0005–10.000	Ni	0.0015–3.20
Cr	0.005–1.500	Zn	0.03–150.00

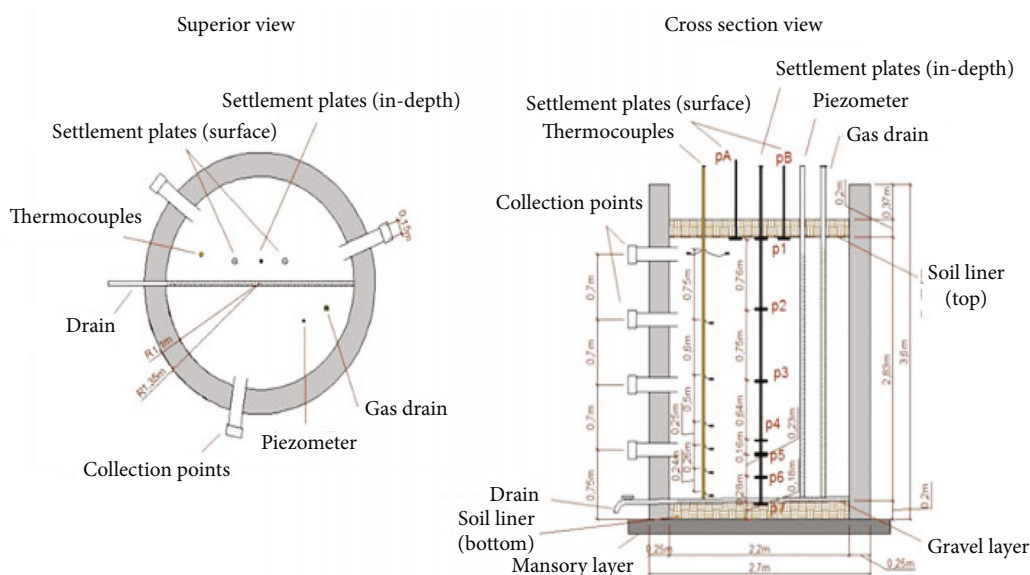Source: adapted from Kjeldsen et al. [46] and Baun and Christensen [47].

FIGURE 1: Schematic section of the experimental cell.

soil layer of 0.25 m with an inclination of 0.5% toward the center of the experimental cell to facilitate the leachate flow. After compacting, the residues were inserted in the cell.

2.1.2. Source of Soil.
The soil selected was analyzed to determine its adequacy to the requirements for use as sanitary landfill liner, such as permeability to water.

Disturbed and undisturbed samples of the investigated soil were collected at a quarry in the rural zone of Boa Vista (state of Paraiba, northeast Brazil), located at coordinates $7^\circ15'41''$ S–$36^\circ14'50''$ W and 480 m above sea level (Figure 2).

Boa Vista region accounts for 60% of the Brazilian bentonite resources. The produced bentonite is mainly used for ceramic production [49]. These bentonitic clays were formed by the alteration of pyroclastic materials derived from volcanic explosions and deposited in depressions previously filled by granular debris with organic activity; subsequent devitrification of vitreous material under alkaline conditions caused the formation of montmorillonite clays and significant silica release [45].

2.2. Adsorption Experiment.
According to the World Reference Base for Soil Resources [50], the soil analyzed is a planosol and alfisol conforming to Soil Taxonomy (1999).

Samples were treated and stored according to ASTM D421-85 [51]. The soil geotechnical, chemical, and mineralogical characterizations were conducted following the methods presented in Table 3.

The solutions were prepared by dissolving 1 g of analytical-grade Cd, Cu, Cr, Pb, Ni, and Zn salts reagents (Impex, Vetec, purity >98%) in distilled water and then diluting these stock solutions 2–16 times in 150 mL of distilled water. The resulting ionic concentrations of the feed solutions are shown in Table 4. Initial pH values lower than 6.0 indicated an acidic environment and consequently high solubility of the metals in the feed solutions.

The batch test of contaminant sorption followed ASTM D4646 guidelines, with a soil-solution ratio of 1 : 12.5 (4 g of dry soil to 50 mL of solution). The suspensions were placed inside 125-mL inert flasks and rotated in an orbital shaker (VWR® Advanced Orbital Shakers, Model 15000) for 24 h at 100 rpm. After 24 h, solid and liquid phases were separated by centrifugation at 3000 rpm for 15 min and filtrated. The filtrates received 5% addition of nitric acid and were maintained at 4°C. The concentration of the metals in the liquid phases was measured by atomic emission spectrometry (Shimadzu, AA-7000).
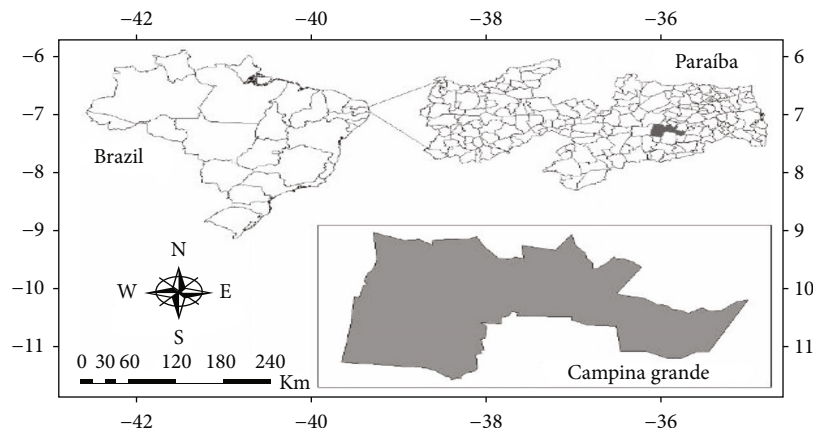
FIGURE 2: Location of the studied area [48].

TABLE 3: Methods for characterization of the investigated soil.

Characteristic	Method
Grain size distribution	ASTM D7928 and ASTM D6913
Specific gravity of solids, G_s	ASTM D854
Liquid limit, w_L	ASTM D4318
Plastic limit, w_P	ASTM D4318
USCS* classification	ASTM D2487
Optimum water content, w_{opt} (proctor standard energy)	ASTM D698
Maximum dry unit weight (proctor standard energy)	ASTM D698
Mineralogical composition	X-ray diffraction
Hydraulic conductivity at optimum water content	ASTM D5856
Chemical composition	X-ray fluorescence
Cation exchange capacity	ASTM D7503
Organic content	ASTM D2974
Electric conductivity	Embrapa [52]
pH in water and in KCl	Embrapa [52]

*Unified Soil Classification System.

The concentration of metals in the solid phases was calculated using Equation (1):

$$S = (C_i - C_e)\frac{V}{m}, \qquad (1)$$

where S is the adsorption degree (mg/g), C_i and C_e are the initial and final (equilibrium) concentrations, respectively (mg/L), V is the volume of solution mixed to the soil (L), and m is the dry mass of soil (g).

Linear, Freundlich, and Langmuir isotherms, expressed in Equations (2), (3), and (4), respectively, were fitted to the experimental data.

$$S = K_d C_e, \qquad (2)$$

$$S = K_F C_e^{1/n}, \qquad (3)$$

$$S = \frac{K_L b C_e}{1 + b C_e}, \qquad (4)$$

where S is the adsorption degree (mg/g), C_e is the equilibrium concentration (mg/L), K_d is the distribution coefficient (L/g), n is a constant related to surface heterogeneity, K_F is the empirical constant of the Freundlich isotherm (L/g), K_L is the equilibrium constant of the Langmuir isotherm (L/g), and b is a constant of the Langmuir isotherm related to the maximum adsorption capacity of the soil (mg/g).

Experimental results of the batch tests were statistically fitted to Equations (2) to (4) using nonlinear least-squares regression by Gauss–Newton algorithm using the software package STATISTICA FOR WINDOWS 12.0. According to Dias et al. [53], this method is more efficient as the linearization of the equations induces errors in the regression analysis and in the estimated parameters of the isotherm models. The implemented number of interactions was 200 with a convergence value of 10^{-6}. Fitting parameters were Pearson correlation coefficient (R^2) and p value with a significance level of $\alpha = 5\%$.

3. Results and Discussion

3.1. Soil Characterization. The geotechnical, chemical, and mineralogical characterization of the soil, which was conducted the following methods indicated in Table 3 is shown in Table 5. The soil was composed of 42% sand, 43% silt, and 15% clay, with a liquid limit of 31%, and a plasticity index of 14%. Considering the Unified Soil Classification System (USCS), the soil was classified as CL.

The clay fraction was mostly smectite (Figure 3). However, the Skempton's activity index (AI) was 0.87, outside the range of 1–7 typical of smectites. Polivanov et al. [55] affirmed that indexes that correlate cation exchange capacity (CEC) and specific surface area (SSA) to clay fraction are more helpful to distinguish mineralogic differences in fine-grained soils than AI. According to Melo and Alleoni [56], these values are within the range of CEC values commonly found in Brazilian soils.

A Skempton's AI of 0.87 indicates a normal clay (AI<0.75 corresponds to inactive clay, with low swelling

TABLE 4: Preparation of feed solutions by adding 1 g analytical-grade reagents to distilled water and dilution.

Metal	Salt	Element concentration (mg/L)					
		Stock solution	Dilution				
			1	2	4	8	16
Cd	$CdCl_2.H_2O$	558	558	280	140	70	35
Cr	$CrCl_3.6H_2O$	195	195	98	49	24	12
Cu	$CuCl_2.2H_2O$	373	373	186	83	47	23
Ni	$Ni(NO_3)_2.2H_2O$	202	202	101	50	25	39
Pb	$Pb(NO_3)_2$	626	626	313	156	78	39
Zn	$Zn(NO_3)_2.6H_2O$	220	220	110	55	28	14

TABLE 5: Soil characterization.

Property	Result	
Soil fractions	Coarse sand	1.0%
	Medium sand	7.0%
	Fine sand	34.0%
	Silt	43.0%
	Clay	15.0%
Specific gravity of the solids, G_s	2.69	
Liquid limit, w_L	31%	
Plasticity limit, w_P	18%	
USCS classification	SC-CL	
Activity index (Skempton)	0.87	
Cation exchange capacity index [54]	1.3	
Optimum water content, w_{opt}	13.4%	
Maximum dry unit weight, γ_{dmax}	19.9 kN/m^3	
Hydraulic conductivity at w_{opt}	4.7×10^{-8} m/s	
Mineralogical composition	Quartz, smectite, and feldspar	
Chemical composition	SiO_2: 54.34%	
	Al_2O_3: 23.07%	
	Fe_2O_3: 8.57%	
	K_2O: 4.46%	
	MgO: 2.78%	
Cation exchange capacity	20.0 cmol$_c$.Kg^{-1}	
Organic content	1.53%	
pH	Distilled water: 8.7	
	KCl: 7.6	

potential in contact with water, and AI>1.25 refers to active clay, with high swelling potential) adequate for compacted clay liners, which are exposed to water content variations and may crack by volume increase.

The high percentages of clay and silt in the soil sample (58%) corroborate the permeability coefficient (10^{-8} m/s). A soil with this coefficient value, according to Junqueira and Palmeira [57] and the standard NBR 13896 [58] is suitable for using as liner material for sanitary landfills. However, Daniel [59] mention that ideal values of bottom layer permeability for soil application in landfills are in the order of 10^{-9} m/s or lower.

The specific gravity of the solids, G_s, was measured as 2.69. Values of organic matter content, CEC, and pH were near the upper limit of typical values for Brazilian soils. According to Embrapa [52], this soil presents low clay activity (CEC<27 cmol$_c$.kg^{-1}); however, this value is above the range of values determined by Fadigas et al. [60] for 162 Brazilian clayey soils, in which 79% exhibited CEC lower than 10 cmol$_c$.kg^{-1} and 96% exhibited CEC lower than 20 cmol$_c$.kg^{-1}. The authors also observed that 89% of the soil samples had pH ≤6, 60% had pH ≤5, and 91% has organic content ≤20 g.kg^{-1}. Therefore, the investigated soil had a pH value higher than that of most Brazilian soils, and the low organic content of 15.3 g.kg^{-1} is consistent with that of the majority of the soils in the country. The net electric charge of the soil estimated through ΔpH ($= pH_{KCl} - pH_{water}$) < 0 indicates the capacity to attract cations (for
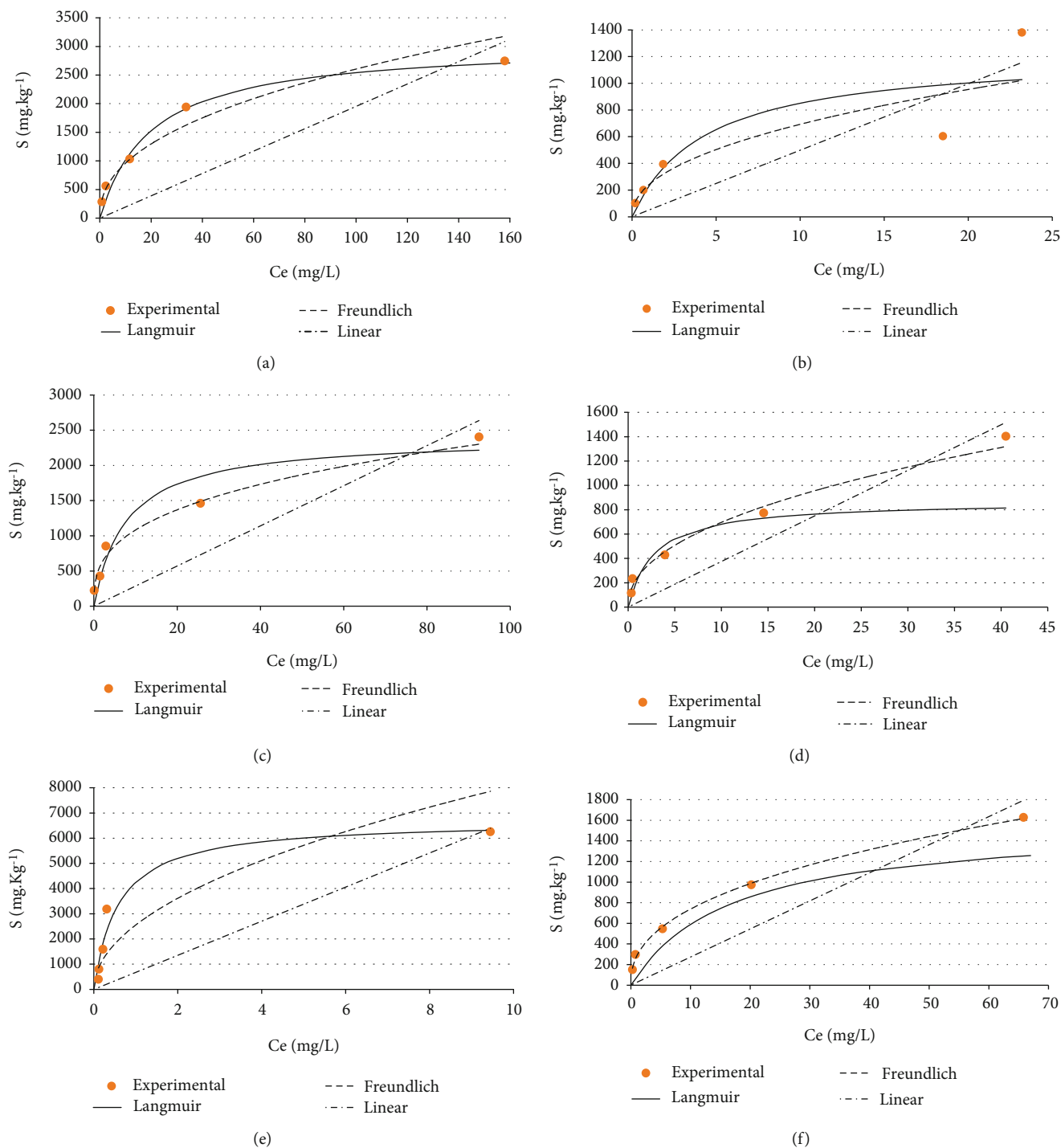
Figure 3: Adsorption isotherms fitted to results of batch tests: (a) Cd; (b) Cr; (c) Cu; (d) Ni; (e) Pb; and (f) Zn.

instance, metallic cations such as the components of the feed solutions for the batch tests).

X-ray fluorescence (XFR) analysis indicated a chemical composition analogous to that of the calcium bentonite characterized by dos Santos and de Lima [61], which had contents of silicon, iron, magnesium, and calcium oxides of 55, 12, 2.65, and 1.26%, respectively. The content of aluminum oxide (23.07%) was similar to that observed in the

chemical composition of Boa Vista bentonitic clays studied by Ferreira et al. [62]. Melo and Alleoni [56] indicated that Fe and Al oxides are predominant in Brazilian soils. These oxides may become electrically active depending on the pH of the interstitial solution (variable charge), significantly contributing with adsorption and promoting the immobilization of toxic metals. During the batch test, the adsorption of metals may have occurred owing to the exchange or

TABLE 6: Statistical analysis of sorption isotherms.

Metal	Model	Coefficients	Estimated value	p-level	R^2
Pb	Linear	K_d(L/g)	0.68	0.019	0.815
	Freundlich	K_f (L/g)	2.83	0.019	0.877
		n	2.79	0.005	
	Langmuir	K_L (L/mg)	1.73	0.034	0.946
		b (mg/g)	6.70	0.001	
Cu	Linear	K_d(L/g)	0.028	0.005	0.815
	Freundlich	K_f (L/g)	0.48	0.284	0.986
		n	2.83	0.150	
	Langmuir	K_L (L/mg)	0.13	0.523	0.931
		b (mg/g)	2.40	0.071	
Cd	Linear	K_d(L/g)	0.02	0.010	0.765
	Freundlich	K_f (L/g)	0.46	0.005	0.969
		n	2.79	0.002	
	Langmuir	K_L (L/mg)	0.05	0.188	0.987
		b (mg/g)	3.05	0.006	
Ni	Linear	K_d(L/g)	0.04	0.020	0.964
	Freundlich	K_f (L/g)	0.25	0.014	0.987
		n	2.38	0.028	
	Langmuir	K_L (L/mg)	0.36	0.061	0.951
		b (mg/g)	0.87	0.003	
Zn	Linear	K_d(L/g)	0.03	0.005	0.957
	Freundlich	K_f (L/g)	0.22	0.000	0.999
		n	2.38	0.000	
	Langmuir	K_L (L/mg)	0.06	0.136	0.975
		b (mg/g)	1.57	0.010	
Cr	Linear	K_d(L/g)	0.05	0.002	0.962
	Freundlich	K_f (L/g)	0.22	0.006	0.781
		n	2.00	0.001	
	Langmuir	K_L (L/mg)	0.23	0.188	0.737
		b (mg/g)	1.22	0.029	

substitution of cations present in the oxides by the heavy metals in the solution. Thus, the presence of both clay minerals and oxides may have eased the adsorption of metals.

Furthermore, the lack of sodium oxide and significant content of magnesium and calcium oxides are in agreement with the chemical composition of calcium bentonite, which shows reduced swelling capacity in contact with water compared to sodium bentonite, having lower AI values (AI < 0.59) such as that of the investigated soil.

3.2. Batch Tests and Adsorption Isotherms. Figure 3 shows the experimental results of the batch tests and fitted isotherms. The estimated parameters of the isotherms and statistical analysis are presented in Table 6. The linear distribution coefficient (K_d) was estimated as 20, 50, 29, 37, 677, 27, and 37 mL.g^{-1} for Cd, Cr, Cu, Ni, Pb, and Zn, respectively. However, as linear isotherms resulted in a poor

fit to the model (R^2 lower than 0.9 except for Ni), these values should be considered as indicatives.

Freundlich model resulted in the highest R^2 values for all elements except for Cd and Ni, for which Freundlich and Langmuir models provided similar R^2 values (Table 6).

Considering the criterion $R^2 \geq 0.9$, the Langmuir model is appropriate for all metals except Cr. This type of isotherm indicates that the sorbed amount tended to stabilize probably due to the occupation of active sites [57]. Furthermore, the adsorption is assumed to be energetically identical at all sites, regardless of molecules adsorbed in the vicinity [63–66].

According to the criterion p < 0.05, the fitting of the Freundlich model to experimental data was acceptable, except for Cr, for which the experimental data was better represented by the linear isotherm. The Freundlich isotherm considers that an almost infinite number of adsorption sites

TABLE 7: Comparison of the cationic heavy metal adsorption capacities of various adsorbents.

Adsorbent	Heavy metal	b (mg/g)	Reference
Acid-activated clay	Ni	0.44	[75]
Bentonite clay from Bhawnagar, India	Pb	19.45	Khan et al., [76]
Bentonite	Ni	13.97	[77]
Bentonite	Ni	26.32	[78]
Bentonite	Cu	17.87	
Bofe bentonite clay	Zn	0.77	Araújo et al., [36]
Magnetic bentonite	Pb	80.40	Zou et al., [79]
Bagasse fly ash	Cd	1.24-2.0	Ahmaruzzaman [80]
Magnetic oak wood biochar	Cd	2.87	Mohan et al. [81]
Treated olive stones	Cd	49.3	Aziz et al. [82]
Magnetic litchi peel	Pb	78.74	Jiang et al. [83]
	Pb	42.50	
Commercial activated carbon	Cu	15.00	Shahrokhi-Shahraki et al. [84]
	Zn	14.00	
Natural zeolite	Cu	0.11	Motsi et al. [85]
	Zn	0.02	
Activated carbon from rice husk	Ni	17.23	Ma et al. [86]
	Cd	29.61	

exist in comparison with the number of species to be adsorbed. Moreover, these species accumulate on the heterogeneous surface of the adsorbent [62, 64, 66, 67]. Additionally, the model also considers that an exponential distribution can characterize the various adsorption sites, which have different adsorption energies [68].

The Cr sorption isotherms fitted better to the linear model, in which, according to Giles [69], the number of sites is considered constant, whereas the sorption by the sorbate increases during the sorption of metallic cations by the soil.

Basso and Kiang [70] obtained K_d, K_f, 1/n, K_L, and b values of 0.3–6.5 mL/g, 44.1 mL/g, 0.59, 0.0087 L/mg, and 0.625 mg/g, respectively, for the adsorption of Cu^{2+} by a clayey young residual soil derived from Itararé Group (lithologic association of sandstone, siltstone, claystone, conglomerate, rhythmite, and diamictite in the central-eastern region of the State of Sao Paulo, located in the southeast of Brazil).

Lima [71] investigated oxisol (LV), entisol (N), and vertisol (V) soils with predominance of fines from the state of Paraná (south Brazil), with CEC values of 13, 23, and 17 $cmol_c \cdot kg^{-1}$, respectively. The adsorption parameters for Cu^{2+} were as follows: $K_f = 0.69$ L/g, 1/n = 0.28, $K_L = 0.15$ L/mg, and $b = 2.3$ mg/g for soil LV; $K_f = 1.38$ L/g, 1/n = 0.23, $K_L = 0.3$ L/mg, and $b = 3.5$ mg/g for soil N; and $K_f = 2.41$ L/g, 1/n = 0.13, $K_L = 0.8$ L/mg, and $b = 4.0$ mg/g for soil V. For a young residual soil derived from granitic gneiss from the state of São Paulo (southeastern Brazil) classified as MH, Stuermer [72] obtained $K_f = 4.5$ mL/g and 1/n = 0.94 for Cd at a pH 3; $K_f = 60.1$ and 1/n = 0.47 for Cd at a pH 5.5; $K_f = 41.1$ mL/g and 1/n = 0.59 for Pb at a pH 3; and $K_f = 160.4$ mL/g and 1/n = 0.33 for Pb at a pH 5.5. The values obtained in the present study for the investigated soil were $K_d = 28.5$ mL/g, $K_f = 0.48$ L/g, 1/n = 0.35, $K_L = 0.13$ L/mg, and $b = 2.35$ mg/g.

Oliveira et al. [73] investigated the adsorption of metals by four soils from the state of Goiás (central Brazil). The obtained values for Cd^{2+} were $K_d = 0.4 – 1.7$ mL/g, $K_f = 1.2–3.0$ L/g, and 1/n =0.59–0.87; for Cr^{6+}, $K_d = 2.6–3.8$ mL/g, $K_f = 4.9 – 5.6$ L/g, and 1/n = 0.82 – 0.88; for Cu^{2+}, $K_d = 1.1 – 2.3$ mL/g, $K_f = 5.5 – 6.5$ L/g, and 1/n = 0.78 – 0.89; for Ni^{2+}, $K_d = 0.6 – 2.5$ mL/g, $K_f = 2.2 – 4.8$ L/g, and 1/n = 0.78 – 0.89; for Pb^{2+}, $K_d = 1.0 – 1.7$ mL/g, $K_f = 2.8 – 5.0$ L/g, and 1/n = 0.80 – 0.93; for Zn^{2+}, $K_d = 0.8 – 1.7$ mL/g, $K_f = 3.7 – 6.9$ L/g, and 1/n = 0.80 – 0.87.

Linhares et al. [74] indicated that the Langmuir and Freundlich models were better suited to the sorption isotherms of Cd and Pb in heavily weathered tropical soils.

Thus, the maximum adsorbent capacities found were similar to those of other Brazilian soils and adsorbents, such as bagasse fly ash and natural zeolite (Table 7). The values were also consistent with those of other bentonites, indicating that the Boa Vista soil can be used as an adsorbent.

The Pb group showed a particularly higher adsorption. Moreover, Cd and Cu exhibited similar behavior, which also occurred for Cr, Ni, and Zn. The different adsorption behavior among cations is commonly a result of valence, atomic mass, and ionic radius differences. Clay minerals demonstrate a higher affinity to higher valence elements. In this study, cations were divalent (Ni = Cu = Cd = Zn = Pb) except for Cr (hexavalent). Elements with a lower ionic radius are preferentially adsorbed among elements of the same valence. The order of atomic radius of the divalent cations analyzed is $Ni^{2+} < Cu^{2+} < Zn^{2+} < Cd^{2+} < Pb^{2+}$, with values 0.615, 0.69, 0.73, 0.74, 0.95, 1.19, and 1.29, respectively [87, 88]. The increasing order of atomic mass for the studied elements is Ni < Cu < Zn < Cd < Pb.

Considering the soil analyzed, these different characteristics resulted in different behaviors, in which Pb was the most adsorbed cation, whereas Ni was the least adsorbed.

4. Conclusions

In this study, the results of experimental tests proved that a bentonitic soil from the Brazilian semiarid region can be used as a low-cost adsorbent, acting in the retention of heavy metals (Cd, Cu, Zn, Ni, Cr, and Pb) in initial concentrations of up to 600 mg/L. The sequence of maximum adsorption capacity for heavy metals followed the series Ni<Cr < Zn < Cd < Cu < Pb. The results indicated that the ion valence and ionic radius were factors that influenced this sequence. Therefore, the soil analyzed has a high potential to be used in the retention of heavy metals and can prevent soil and groundwater contamination problems in landfill areas.

Data Availability

Data are available on request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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