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Study of Potentially Toxic Metal Adsorption in a Polluted Acid and Alkaline Soil: Influence of Soil Properties and Levels of Metal Concentration

Evangelia E. Golia [1,*], Ourania-Despoina Kantzou [1,2], Maria-Anna Chartodiplomenou [2], Sotiria G. Papadimou [1] and Nikolaos G. Tsiropoulos [3]

[1] Laboratory of Soil Science, School of Agriculture, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece
[2] Laboratory of Soil Science, Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 384 46 Volos, Greece
[3] Analytical Chemistry and Pesticides Laboratory, Department of Agriculture Crop Production and Rural Environment, University of Thessaly, Fytokou Street, 384 46 Volos, Greece
* Correspondence: egolia@auth.gr; Tel.: +30-2310-998-809

Abstract: In the present study, the adsorption of zinc (Zn), lead (Pb), copper (Cu), and cadmium (Cd) was studied in two already polluted urban soil samples with different pH values, an acidic and an alkaline one. The Langmuir and Freundlich adsorption isotherm equations were used to thoroughly study the adsorption of the metallic elements on the solid surface of the soils. Langmuir equation described the adsorption of each metal satisfactorily, with a slight predominance over Freundlich, in both soils, as the R^2 value approached almost unity. Even though Zn and Cu were adsorbed on the soil phase, their adsorption was minimal compared to the adsorption of more harmful metals such as Pb and Cd. Using the values of the coefficients obtained from the equations of the mathematical models, we concluded that in alkaline soils, the retention of metals was much greater than in acidic soils. The simultaneous presence of metals during the addition of the single-element solutions of the metals to the already metal-contaminated soils caused competitive adsorption increasing the retention of the more toxic metals on the solid surface of the alkaline soil. Factors affecting soil sorption (such as soil pH and $CaCO_3$ content) were studied to provide theoretical support for understanding the laws and causes of metal sorption in the soils of the survey.

Keywords: heavy metal retention; Langmuir; Freundlich; adsorption isotherms; competitive adsorption

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1. Introduction

Soil can be defined as a physical body that occurs as a result of rock and mineral decomposition, providing mechanical support and a perfect background for plant nutrition [1,2]. It is the upper layer of the earth where plants grow, a black or dark brown material typically consisting of a mixture of organic remains, clay, and rock particles [3]. In 2013, the International Organization for Standardization [4] defined soil as the uppermost layer of the earth's crust transformed by weather conditions and physical, chemical, and biological processes. The more appropriate the management of the soil, the better the production of high-quality food for the world's ever-increasing population [5,6]. Due to the constant technological evolution and the economic development of many fields, such as the industrial, the environment is becoming more polluted [7,8]. In recent decades, the risk of heavy metal pollution of the environment has been increasing and causing greater concern for the environment and human health [9].

Heavy metals are a large group of metallic elements with a high atomic weight and a density greater than 5 g cm^{-3} that are of great industrial and biological interest [2]. Their existence is due to various sources, they may have a geochemical origin, but they also come from a variety of anthropogenic activities, such as industry, mining, and agriculture [10]. Soil pollution in rural environments is due to the reckless use of fertilizers, the use of animal manure, and the use of solid and liquid wastes in agriculture [11–13]. It can be perceived that heavy metals, whether of natural or anthropogenic origin, are the most toxic inorganic pollutants appearing in both aqueous and soil environments [10,14]. This is mainly because they do not biodegrade through natural processes, have long half-lives, and are particularly dangerous pollutants as they enter the food chain [3]. This fact indicates the necessity and the urgency of their removal. At present, various methods of controlling or reducing heavy metal concentrations from surface water are being carried out, such as chemical precipitation, ultrafiltration, adsorption, reverse osmosis, coagulation, and flocculation [15,16]. Among them, adsorption is characterized by many desirable properties, such as high removal efficiency, low cost, and being friendly to the environment with a low footprint [17].

Adsorption is a physicochemical process where a gas or liquid solute accumulates on the surface of a solid or liquid, forming a molecular or atomic film [18]. This kind of process can be observed at the interface of any two phases, such as at the interface of liquid–liquid, gas–liquid, gas–solid, or liquid–solid. In environmental geochemical systems, adsorption reactions at soil interfaces play a decisive role in the mobility, speciation, and bioavailability of trace elements and toxic pollutants [19,20]. The surface of the solid or liquid that adsorbs the gas or liquid solute constitutes the "adsorbent," while the molecular or atomic film formed is the "adsorbed." This process is usually caused due to physical forces or chemical bonds and can be reversed [21]. The reverse process is called "desorption," while the term "sorption" includes both processes [22,23]. The process of adsorption is described with certain equations that estimate the amount of the adsorbed solute on the surface of the adsorbent per unit weight as a function of equilibrium concentration at a constant temperature [11,24,25]. These equations are called isotherms due to the dependence of their parameters on temperature, which consists of one of the most important environmental factors affecting adsorption. The most used isotherms to describe adsorption are the Langmuir and Freundlich isotherms due to their relative simplicity and reasonable accuracy [26]. The Langmuir isotherm is a simple type of adsorption equilibrium model that can be applied at both high and low pressures [27] and is commonly used when there is ideal monolayer adsorption on a homogeneous surface [28]. Moreover, it is used to describe the behavior of many systems, such as the adsorption of non-polar gases on activated carbon and zeolites [8]. On the other hand, the Freundlich isotherm is usually suitable for non-ideal adsorption on heterogeneous surfaces while also determining the heterogeneity of this surface. This model assumes the existence of a large number and many different types of sites acting simultaneously, each with a different free energy of adsorption, and can determine the exponential distribution of these active sites and their energies [28,29]. The most significant and used parameters of these models are the Langmuir maximum adsorption capacity (q_{max}) and the Freundlich constant coefficient associated with the distribution coefficient (K_F) [30]. The study of the adsorption of metals in soils containing single or more than one metal has been done by many researchers [31,32]. However, the study of the effect of competitive adsorption of Zn, Pb, Cu, and Cd in urban Mediterranean soils that are naturally contaminated with metals and have different physical and chemical properties is of particular interest.

The present study serves as a solid framework that could be used to adequately describe, capture, and even prevent the soil pollution of metals in the studied area. Four common metals present in urban soils were selected, two of them being toxic (Cd and Pb), while Cu and Zn in low concentrations are essential for the normal functioning of living organisms. In addition, the adopted methodology of metal adsorption could be generalized spatially and temporally, as it could be applied in alkaline soils moderately polluted with heavy metals and in climatic conditions similar to those prevailing in a Mediterranean environment as in the study area (central and northern Greece).

2. Materials and Methods

2.1. Adsorption Study

The adsorption of Zn, Pb, Cu, and Cd was measured in two different urban soils, acidic and alkaline, obtained from the areas of northern and central Greece, respectively. The adsorption of the metals in the two soils was assessed using the standard batch equilibration method [33]. Triplicates for each metal and concentration level were studied. The Langmuir and Freundlich isotherm models were used to examine metal adsorption by the two soils.

2.1.1. Preparation of Solutions and Adsorption Experiments

The background electrolyte $CaCl_2$ solution was prepared by dissolving 1.47 g of solid $CaCl_2$ $2H_2O$ in 800 mL of deionized water, and then the contents were transferred to a 1000-mL volumetric flask, which was made up to the mark with deionized water. Thus, the prepared 0.01 M solution was stored in 1000 mL plastic bottles, and the process was repeated until enough was prepared to create a solution at specific concentrations of copper, cadmium, zinc, and lead.

For the adsorption study using the batch equilibrium method, a solution of 1000 mg L^{-1} of each metal was prepared from the metal salt that has the same anion as that of the background electrolyte. A proper quantity of each metal chloride salt was dissolved in one liter of 0.01 M $CaCl_2$ into different prepared solutions with concentrations of 5, 10, 20, 40, 60, 80, and 100 mg L^{-1} for each metal.

Once the preparation of the solutions was completed, a quantity of 2 g of soil from each soil sample was weighed on a precision electronic balance (0.01 g) in 50 mL falcon vials. Then, to each of them, achieving a ratio of 1:10, 20 mL of metal chloride solution with an initial concentration of Co = 5, 10, 20, 40, 60, 80, and 100 mg L^{-1} was added and shaken in a reciprocating shaker for 16–24 h. After shaking and once equilibration had been achieved, the suspensions were filtered into clean 50 mL falcon flasks using slow filter papers. The unknown C concentration of the resulting extract contains the metal studied and is the equilibrium concentration [34]. The difference between the equilibrium and the initial concentration constitutes the amount of metal adsorbed from the soil and is denoted by q. The q value was calculated based on the following formula:

$$q = (Co - C) \times (V/W) \tag{1}$$

where V = the volume of the solution in the falcon vial and W = the mass of soil in the falcon vial. Finally, the adsorption of each metal was determined using an atomic absorption spectrophotometer.

2.1.2. Competitive Adsorption

In order to find the effect of the simultaneous presence of two metals, a bimetallic metal system was used for the adsorption experiments on the two soils. To carry out the bimetallic adsorption experiments, equal volumes of solution at twice the concentration were used so that the final concentration of each metal was equal to the initial one. In this way, the results were comparable to single-element adsorption experiments in both alkaline and acidic soil.

2.1.3. Freundlich Isotherm

The Freundlich adsorption isotherm has the form [34]:

$$q = K_F \times C^{1/} \tag{2}$$

where

q (mg kg^{-1}) is the amount of metal adsorbed per kg of soil,
C (mg L^{-1}) is the metal concentration in solution at equilibrium,

K_F (mg $^{1-1/n}$ (L)$^{1/n}$ Kg^{-1} is a constant called the Freundlich adsorption coefficient and indicates the adsorption capacity of the adsorption process. The K_F constant depends on temperature and is only a qualitative indicator of the adsorption capacity of the adsorbent.

n is the regression constant. Constant *1/n* of the Freundlich adsorption isotherm is a dimensionless parameter expressed with the adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites of the material, i.e., in the specific case of the soil. Its values range from zero to one, and the closer they are to unity, the more homogeneous the adsorbent material is. In the present study, as already mentioned, the sorbent material is the soil, which suggests that no value of *1/n* will equal unity since urban soil is inherently heterogeneous [3].

2.1.4. Langmuir Isotherm

The Langmuir adsorption isotherm has the form:

$$q = (q_{max}\ K_L\ C)/(1 + K_L\ C) \tag{3}$$

where

- q_{max} (mg kg^{-1}) is a constant that expresses the maximum concentration of the studied metal that can be adsorbed to the soil,
- q (mg kg^{-1}) is the amount of metal adsorbed per kg of soil,
- C (mg L^{-1}) is the metal concentration in solution at equilibrium and
- K_L (L kg^{-1}) is the Langmuir constant, which, however, expresses the degree of affinity of adsorption sites.

Due to the complexity of the above equation, it is necessary to "linearize" it, that is, to simplify it in such a way that the final relation has the form y = ax + b. Thus, the Langmuir adsorption isotherm expression becomes $1/q = [1/(q_{max}\ K_L)] \times (1/C) + 1/q_{max}$. Therefore, $a = 1/(q_{max}\ K_L)$, $b = 1/q_{max}$ and $K_L = b/a$.

2.2. Physicochemical Analyses of Soil Samples

The two soil samples used for the adsorption experiments were air-dried and sieved with a 2 mm diameter sieve. After that pretreatment, they were disposed for chemical analyses as follows [35]: for the determination of soil pH and electrical conductivity (EC) values, a soil solution ratio of 1:1 was used [36]. Particle size distribution was measured using the Bouyoucos method [37], while the organic carbon content was conducted using the wet digestion method (Walkley–Black). The cation exchange capacity of the soil samples was calculated as the sum of the concentrations of the exchangeable ions (Na^+, K^+, Ca^{2+}, Mg^{2+}) of the soils. The exchangeable ions were extracted with a CH_3COONH_4 solution, 0.1 M (pH = 7), while their quantification was accomplished using a flame photometer.

The available metal concentration was determined after extraction with DTPA solution in a ratio of 1:2 (soil: DTPA solution). Total metal concentrations were measured using the Aqua Regia method [4]. The concentrations of all the metals studied were determined using atomic absorption spectrophotometry (AAS) with flame and/or the Graphite Furnace techniques [38,39] according to their detection limits. Analytical-grade chemical reagents were used for the digestion and laboratory analyses. Metals standard solutions (1000 mg L^{-1}) were prepared from Merck "titrisol" after a series of properly diluted solutions.

For the evaluation of the analytical methods, a Certified Reference Material (CRM) (No 141R, calcareous loam soil) from BCR (Community Bureau of Reference) was analyzed with the soil samples. The recovery ratio ranged from 85.1% to 104.3%.

3. Results and Discussion

3.1. Physicochemical Properties of Soils

The values of the physicochemical parameters, along with the total and available metal concentrations of the two contaminated soils used for the adsorption study, are presented in Table 1. The two soils differ significantly as far as their pH value is concerned, as one has an acidic reaction while the other is alkaline. The difference in reaction also leads to a statistically significant difference in %$CaCO_3$ content. It is well known that the majority of soils located in an urban environment are alkaline [24]. Alkaline soil has calcium carbonate at a percentage of 7.7%, while no $CaCO_3$ was detected in acidic soil.

Table 1. Physicochemical parameters, total and available metal concentrations (mg kg^{-1}) of soil samples. ND: not detected.

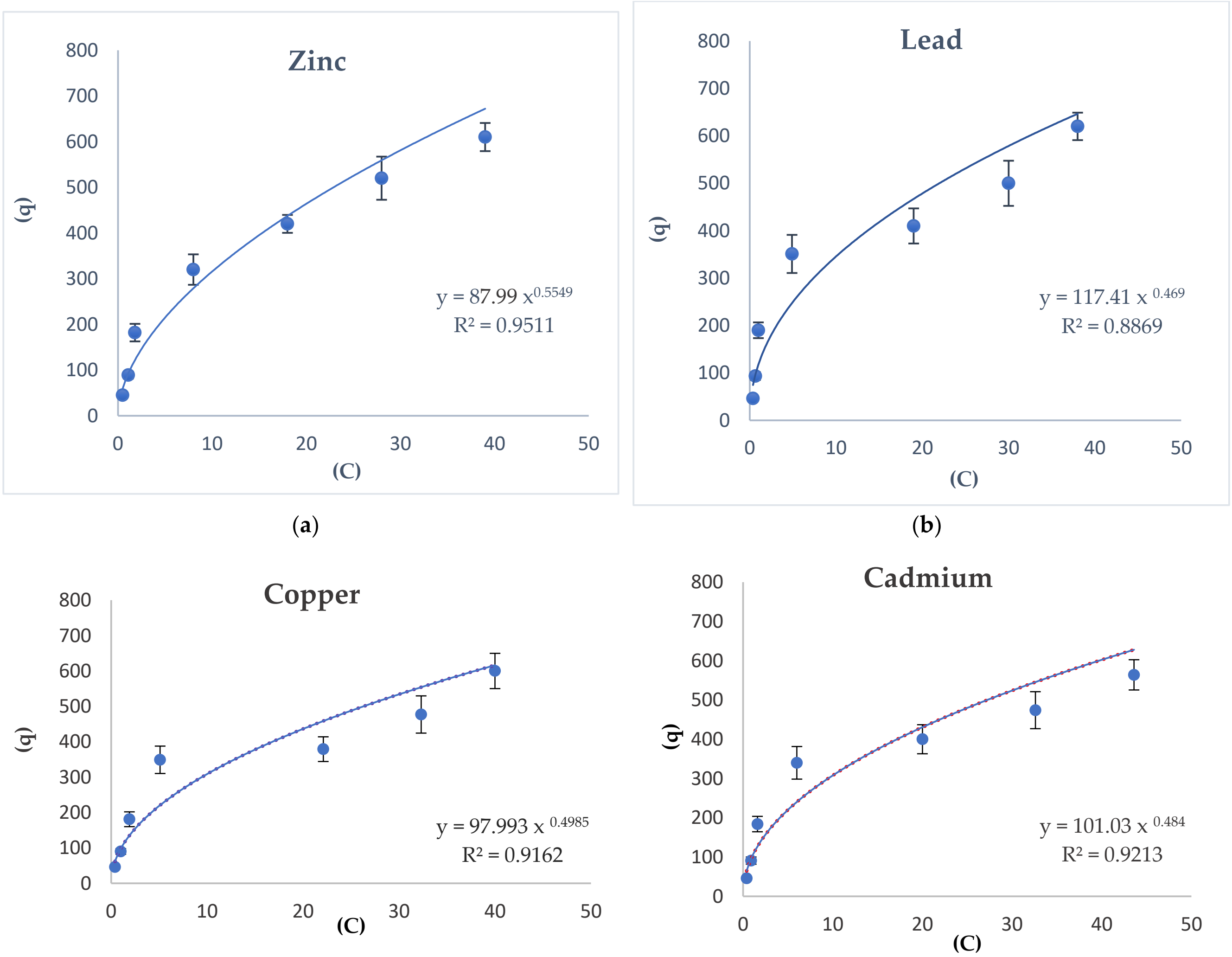
Title 1	Alkaline Soil	Acidic Soil
pH (1:1)	8.3 ± 0.5	5.9 ± 0.3
EC (μS cm^{-1})	1281 ± 64	1445 ± 24
Clay (%)	39.1 ± 0.4	42.1 ± 0.8
Sand (%)	21.7 ± 1.1	23.7 ± 2.4
CaCO3 (%)	7.7 ± 0.9	ND
CEC (cmolc kg^{-1})	31.3	22.1
Zn (Total) (mg kg^{-1})	45 ± 2.9	39.3 ± 2.6
Zn (available) (mg kg^{-1})	3.7 ± 1.1	2.7 ± 2.1
Pb (Total) (mg kg^{-1})	4.5 ± 1.1	3.8 ± 2.2
Pb (available) (mg kg^{-1})	0.7 ± 3.2	0.9 ± 4.1
Cu (Total) (mg kg^{-1})	23 ± 2.4	21.3 ± 1.7
Cu (available) (mg kg^{-1})	2.2 ± 3.2	2.2 ± 4.3
Cd (Total) (mg kg^{-1})	1.1 ± 0.3	0.9 ± 0.2
Cd (available) (mg kg^{-1})	ND	ND

The two soils have almost equal values of electrical conductivity (EC) and the same mechanical composition, as they present the same percentages of sand, silt, and clay (%). The two soil samples collected from northern and central Greece are moderately polluted. They have similar values for total and available concentrations of Zn, Pb, Cu, and Cd (Table 1).

3.2. Adsorption of Zn, Pb, Cu, and Cd Using the Freundlich Model

Figure 1 shows the adsorption of Zn, Pb, Cu, and Cd in the alkaline soil sample. As shown, the R^2 that has a fairly high value (0.9511, 0.8869, 0.9162, 0.9213, respectively) approaching the unit indicates a high correlation between the experimental data and Freundlich adsorption model and suggests that the proposed model satisfactorily describes the adsorption phenomenon. The K_F values of Zn, Pb, Cu, and Cd are 87.99, 117.41, 97.99, and 101.03, respectively. The calculated K_F constants are only a qualitative indication of the adsorption capacity of metals in soils. From the study of the Kf values, there seems to be a stronger adsorption tendency of the more toxic elements (Pb & Cd) than of the less toxic (Zn & Cu) in alkaline soil. However, the mathematical equations of the Langmuir equation were used to find the maximum amount of adsorption, as in numerous similar studies [29,31] of metal adsorption in various soil types.

Figure 2 shows the adsorption of Zn, Pb, Cu, and Cd in the acidic soil sample. As seen, the R^2 that has a high value (i.e., 0.9618, 0.9353, 0.9845, and 0.9496, respectively) approaching the unit indicates that the adsorption was relatively successful. Regarding the K_F values, as shown by the equation in the graphs, the adsorption capacity of the metals follows the order: Cd > Zn > Pb > Cu, as they have the following K_F values 68.90, 58.99, 58.84, and 53.10, respectively.



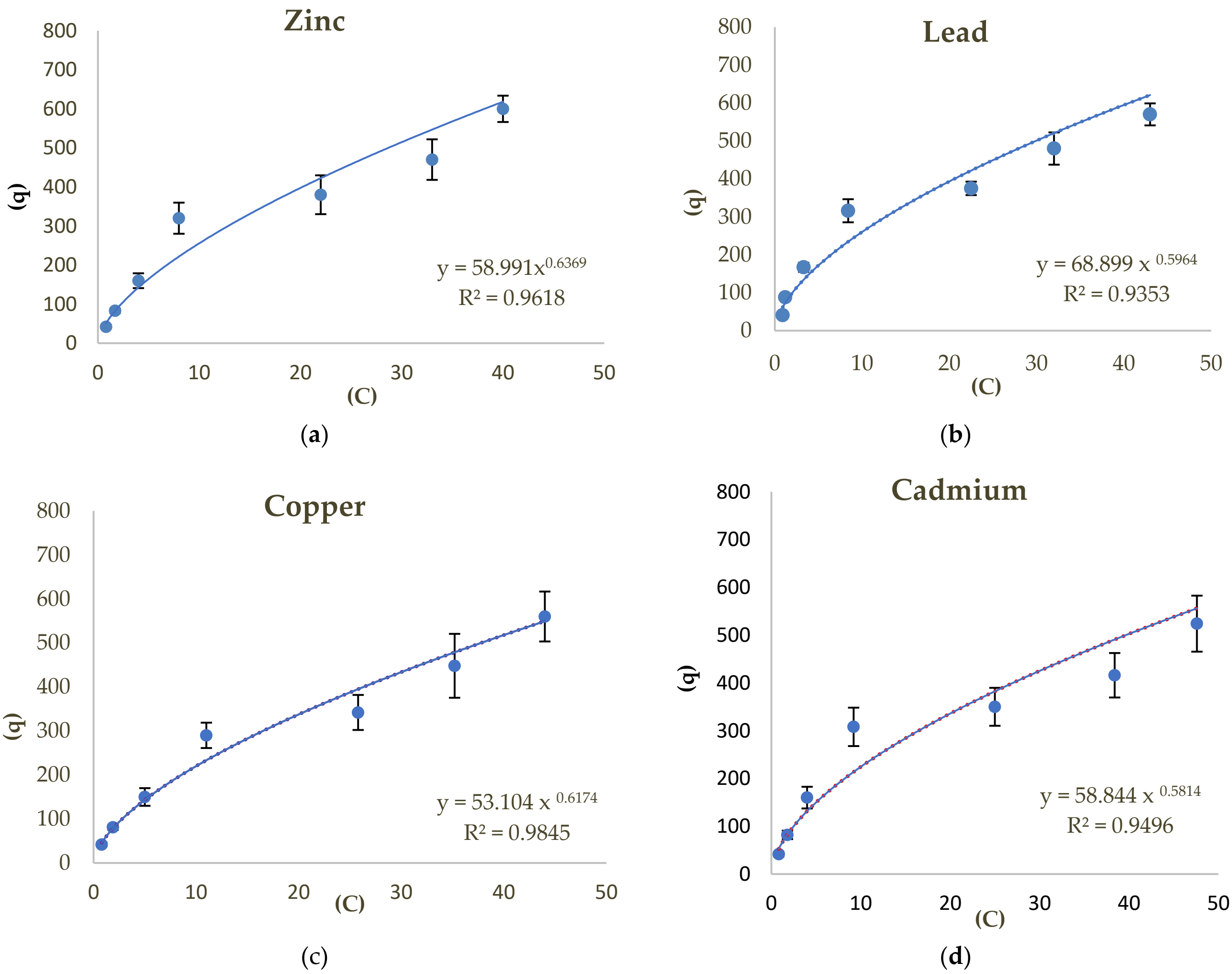
(**a**) (**b**)

(c) (**d**)

Figure 1. The *Freundlich isotherm* adsorption of Zn, Pb, Cu, and Cd (**a**–**d**)in the alkaline soil sample.

Using the Freundlich isotherms, it seems that they satisfactorily describe the adsorption phenomenon of all four metals. Adsorption of the four studied metals appears to be much greater in alkaline soil. Comparing the difference in the values of the K_F coefficient between the alkaline and acidic soil for each metal, we observe that the largest value is presented by the adsorption capacity of Pb, while the smallest is presented by the adsorption capacity of Zn. The difference in the adsorption intensity coefficient between the alkaline and the acidic soil follows the following order: Pb > Cu > Cd > Zn. This means that the effect of soil pH is greater with regard to the adsorption of Pb in the solid phase of the soil. Campillo-Cora et al. [31] presented the same results when studying the adsorption of metallic elements in soils, explaining mono- and multi-element adsorption experiments.

The calculated *1/n* values for all the metals from the Freundlich isotherms (Figures 1 and 2, Table 2) lie between 0.469 and 0.555 in alkaline soil and between 0.581 and 0.637 in acidic soil showing high heterogeneity in the adsorption sites.



(**a**) (**b**) (c) (**d**)

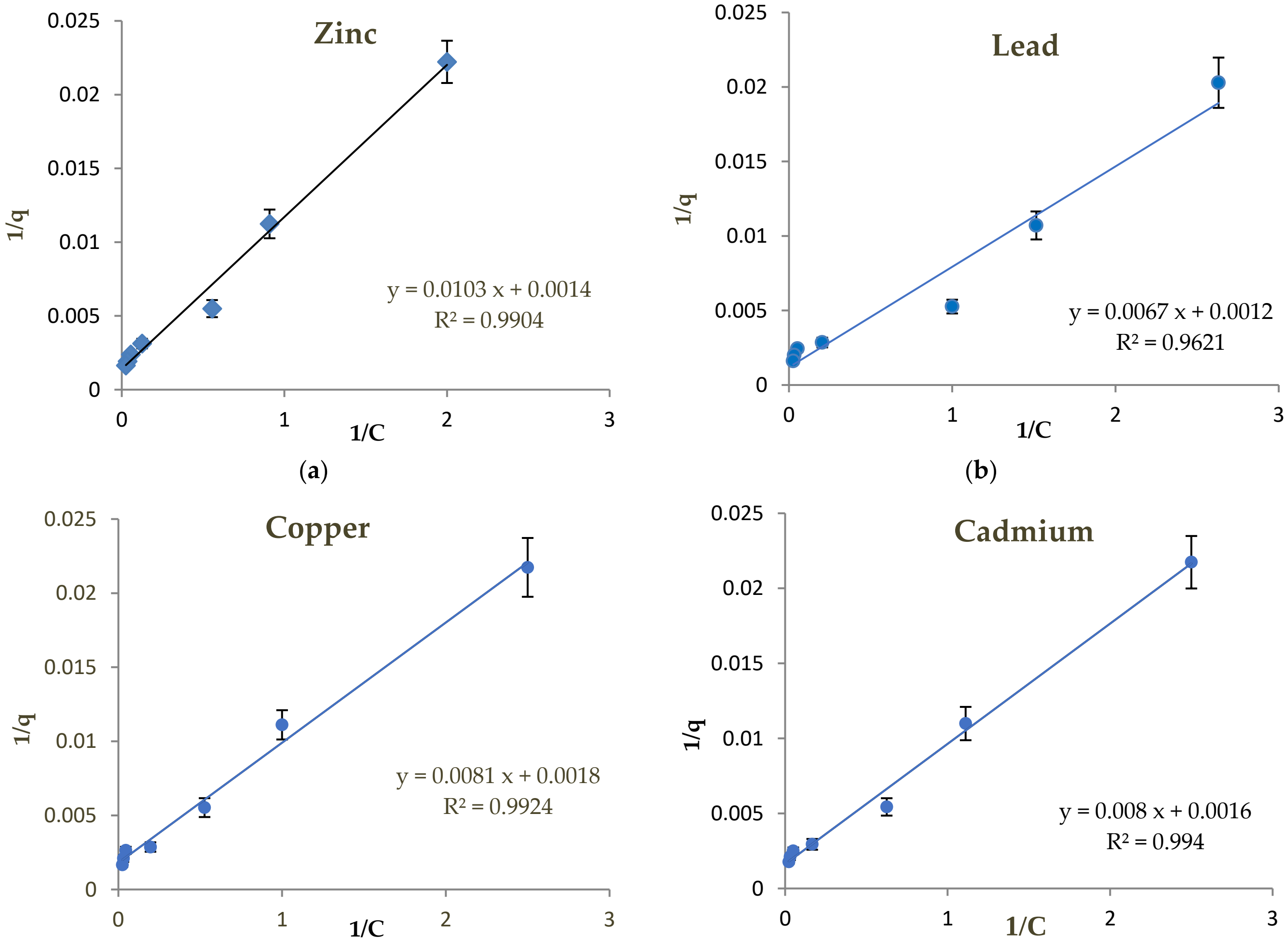
Figure 2. The *Freundlich isotherm* adsorption of Zn, Pb, Cu, and Cd (**a**–**d**) in the acidic soil sample.

Table 2. Freundlich and Langmuir isotherm parameters for Zn, Pb, Cu, and Cd in both studied soils.

		Freundlich Parameters			**Langmuir Parameters**		
		1/n	**K_F (mg kg^{-1})**	**R^2**	**q_{max} (mg kg^{-1})**	**K_L (L kg^{-1})**	**R^2**
Alkaline soil	Zn	0.555	87.99	0.9511	714.3	0.14	0.9904
	Pb	0.469	117.41	0.8869	833.3	0.18	0.9621
	Cu	0.499	97.99	0.9162	555.6	0.22	0.9924
	Cd	0.484	101.03	0.9213	625.0	0.20	0.9940
Acidic soil	Zn	0.637	58.99	0.9618	555.6	0.11	0.9922
	Pb	0.596	68.90	0.9353	909.1	0.062	0.9157
	Cu	0.617	53.10	0.9845	476.2	0.12	0.9928
	Cd	0.581	58.84	0.9496	588.2	0.094	0.9987

3.3. *Adsorption of Zn, Pb, Cu, and Cd Using the Langmuir Model*

Figure 3 shows the adsorption of Zn, Pb, Cu, and Cd in the alkaline soil sample. As shown, the trend line is linear, and the R^2 that has a fairly high value (0.9904, 0.9621, 0.9924, 0.9940, respectively) approaching the unit indicates that the adsorption was successfully described by the Langmuir isotherm. The K_L values for Zn, Pb, Cu, and Cd are 0.14, 0.18, 0.22, and 0.20, respectively (Table 2). The K_L expresses the degree of affinity of adsorption sites of the soil samples studied, and therefore in alkaline soil, there appears to be a greater affinity for the retention of lead, copper, and cadmium than for zinc.



(**a**) (**b**)

(**c**) (**d**)

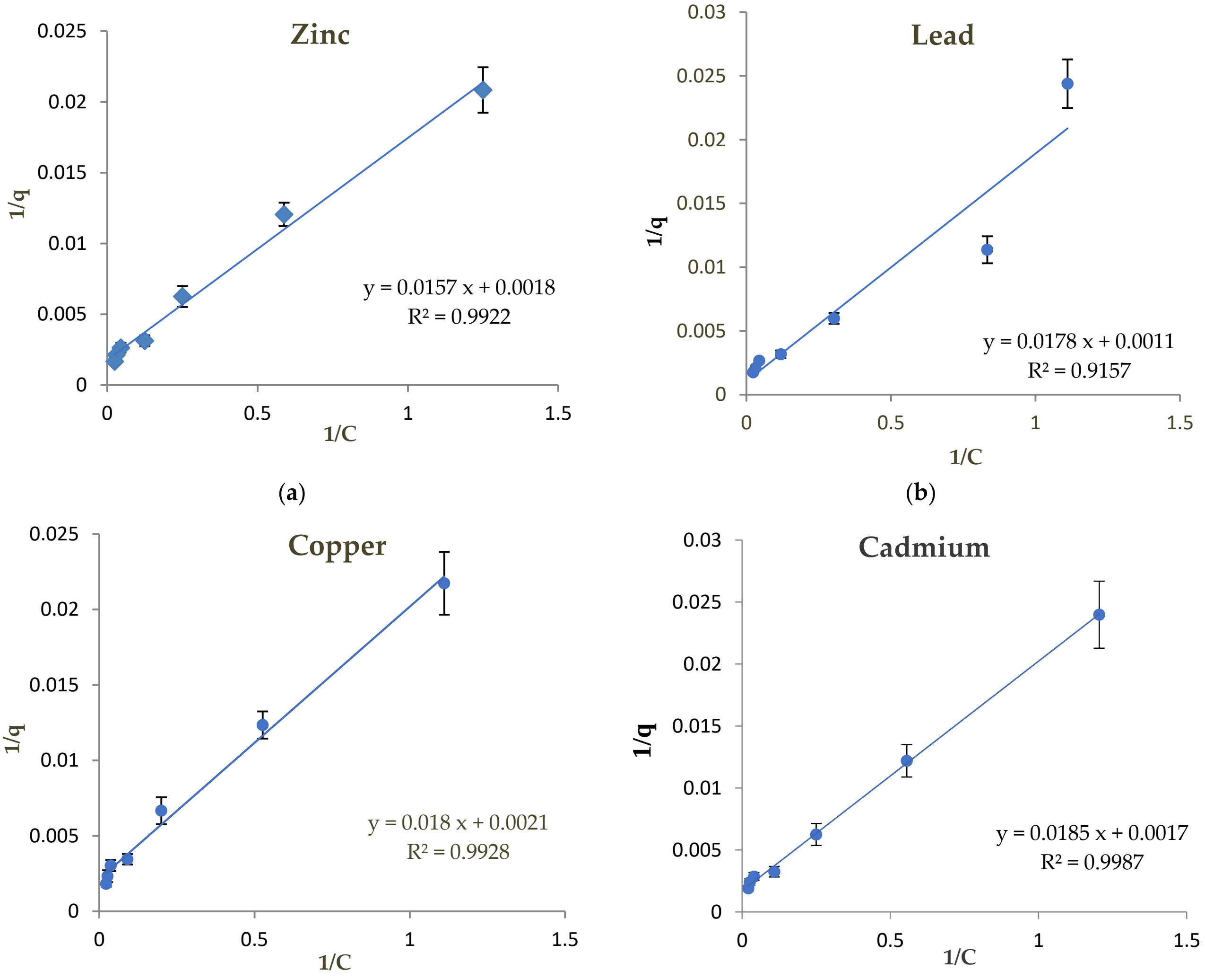
Figure 3. The *Langmuir isotherm* adsorption of Zn, Pb, Cu, and Cd (**a**–**d**) in the alkaline soil sample.

Figure 4 shows the adsorption of Zn, Pb, Cu, and Cd in the acidic soil sample. As it appears, the trend line is linear, and the R^2 has fairly high values of 0.9922, 0.9157, 0.9928, and 0.9987, respectively, indicating that the adsorption phenomenon was successfully described. The values of K_L are equal to 0.11, 0.062, 0.12, and 0.094 for Zn, Pb, Cu, and Cd, respectively (Table 2). Regarding the affinity of the metals with the solid surface of the acidic soil sample, we observe that the most toxic metals appear to be retained more loosely than the less toxic ones. Thus, lead is held less strongly than zinc, and cadmium less strongly than copper. So, in acidic soil, the most toxic elements (Pb and Cd) appear to be even more dangerous than if they were in alkaline soil and had equal concentration [40,41].

3.4. Comparison of Freundlich and Langmuir Isotherms

In Table 2, the isotherms parameters for each metal in both soil samples are presented. For the study of the Freundlich isotherm model, the values of the constant *1/n* and the coefficient K_F are presented, while for the Langmuir isotherm, the values refer to the constant q_{max} and K_L.

Comparing the K_F values of the Freundlich isotherm for the metals between the two soils, it seems that those of the alkaline soil are 1.5–1.8 times higher than those of the acidic soil. This fact indicates that alkaline soil has a higher adsorption capacity, which also depends on the pH value [41]. In addition, the *1/n* values obtained for all metals studied are about 25% higher in the acidic soil than in the alkaline one. This leads to the conclusion that the adsorption intensity in acidic soil is significantly higher than in alkaline soil, as the *1/n* value and adsorption intensity are proportional [33]. In a qualitative assessment, the Freundlich model provided an estimation of both the adsorption capacity and the adsorption intensity of the soils, while the Langmuir equation was used to calculate the maximum amount of metal adsorption in the two soils.



(**a**) (**b**)

(**c**) (**d**)

Figure 4. The *Langmuir isotherm* adsorption of Zn, Pb, Cu, and Cd (**a**–**d**) in the acidic soil sample.

Studying the parameters of the Langmuir isotherm model, we observe that the q_{max} values of Zn, Cu, and Cd in the alkaline soil are higher than those in the acidic soil. However, this is not observed in the Pb isotherm, as the q_{max} in acidic soil is slightly higher compared to that in alkaline soil. This is likely to be due to the competitive phenomena that develop due to the simultaneous presence of other metals, as the soils were already contaminated [1–3].

The values of K_L of Zn Langmuir isotherms are almost equal in both soils. On the other hand, the values of K_L of Pb, Cu, and Cd in the Langmuir isotherm model are clearly lower in acidic soil than in alkaline soil, which suggests that this metal is better retained and more strongly in the soil sample at $pH > 7$. Adamczyk-Szabela and Wolf [42] extensively studied the effect of soil pH on the retention of metals in the solid phase of the soil and, therefore, on their availability to plants. In alkaline soils, generally, the retention mechanisms of metals on the solid surface are activated, as the number of sites that metal ions can occupy appears to increase [2]. In acidic soils, on the contrary, the retention of metals occurs on a smaller scale [23,24].

The K_F values of Cu and Cd, in Freundlich equations, do not differ statistical significant, both in the alkaline and the acidic soil. However, the almost double K_F value of copper and cadmium in the alkaline soil sample compared to the acidic one indicates its highly dependent relationship with the soil pH. Regarding the Langmuir isotherm, the maximum concentration (q_{max}) of copper and cadmium is higher when the soil pH is alkaline. The values of the K_L constant of all the metals in the study in acidic soil were found to be lower than those of alkaline. This leads to the conclusion that the metals were adsorbed more loosely in the acidic soil, as their retention energy from the solid soil surface was significantly lower.

Arias et al. [15] studied the adsorption of metallic elements in acidic soil and also found that it was relatively small. However, it depended on the physicochemical characteristics of the soil, such as the percentage of clay and the mineralogical composition of the soil [33]. The low adsorption capacity of metals in acidic soil may explain the increase in their availability as the soil pH value decreases [24]. The tendency of soils to adsorb more Pb than less toxic elements, such as Cu, was also observed in the work of Elbana et al. [32] in both acidic and alkaline soils.

3.5. Competitive Adsorption of Metals in the Soil Samples

Figures 5–8 show the adsorption curves of the metals Zn, Pb, Cu, and Cd, in bimetallic pairs. In Figures 5a,6a,7a, and 8a, the curves relate to the study of the phenomenon of the adsorption of the bimetallic pairs Zn–Pb, Pb–Zn, Cu–Cd, and Cd–Cu in the alkaline soil. In the corresponding images with index b, the phenomenon is studied in acidic soil.

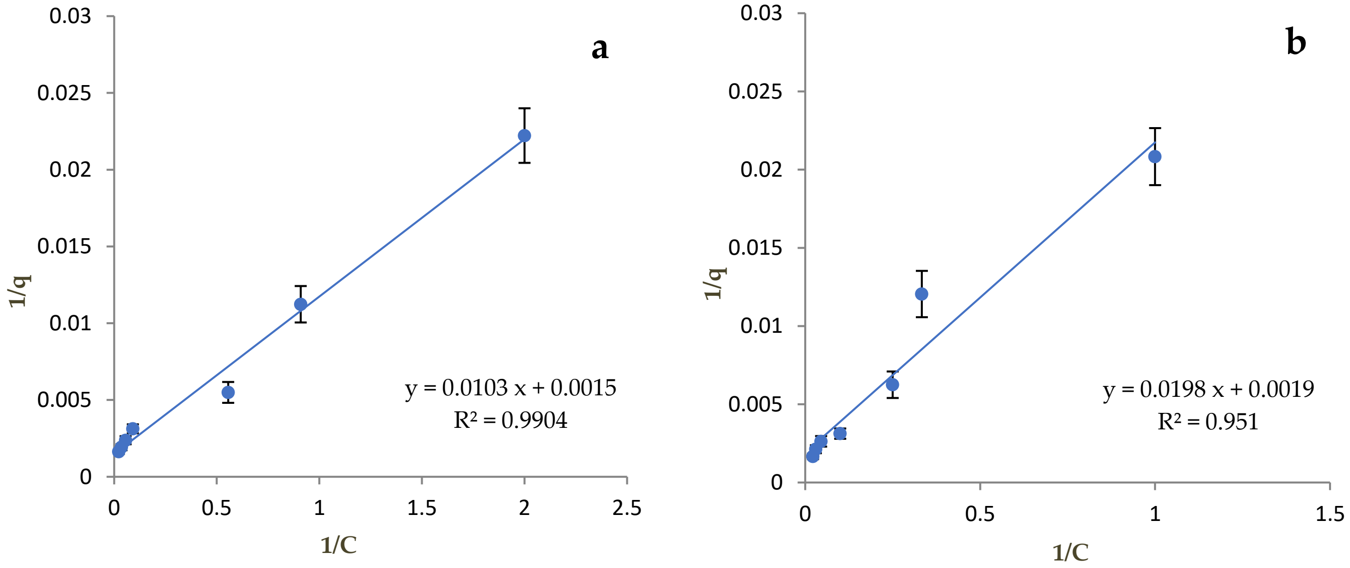


Figure 5. The *Langmuir isotherm* adsorption of Zn in the presence of Pb in the alkaline soil sample (**a**) and in the acidic soil sample (**b**).

In Table 3, the Langmuir isotherm absorption parameters for Zn and Pb, and for Cu and Cd during the bimetallic system of both studied soils, are presented. The study of the phenomenon of bimetallic adsorption was accomplished using the Langmuir equations in order to determine the maximum values of the metals adsorbed in each case.

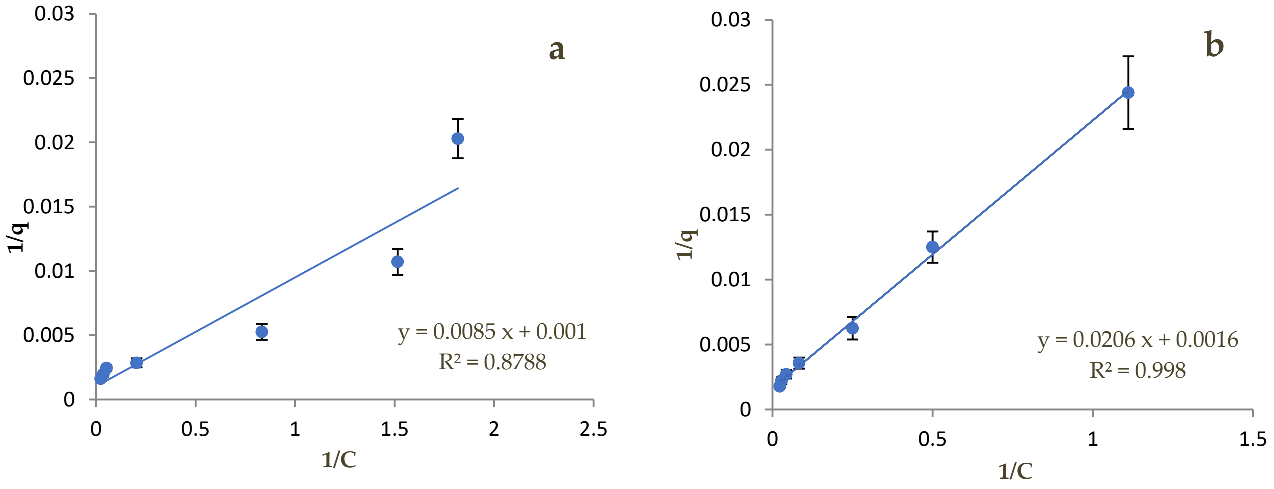


Figure 6. The *Langmuir isotherm* adsorption of Pb in the presence of Zn in the alkaline soil sample (**a**) and in the acidic soil samples (**b**).

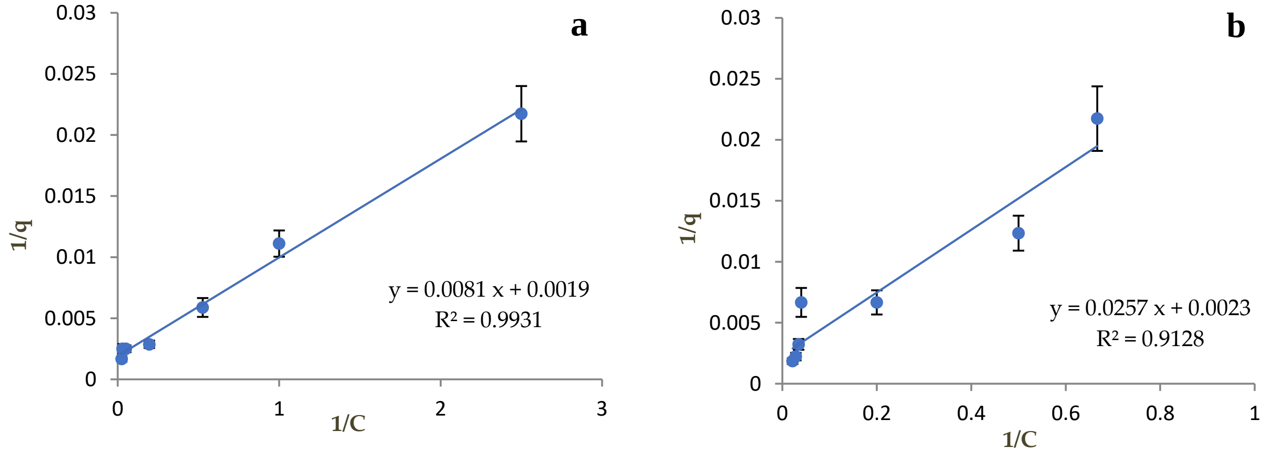


Figure 7. The *Langmuir isotherm* adsorption of Cu in the presence of Cd in the alkaline soil sample (**a**) and in the acidic soil samples (**b**).

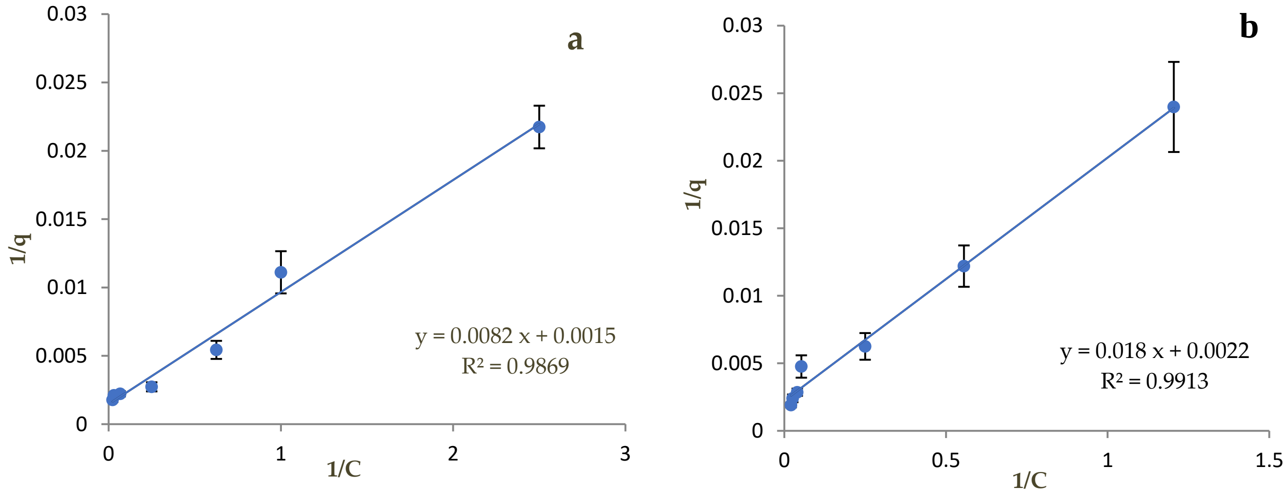


Figure 8. The *Langmuir isotherm* adsorption of Cd in the presence of Cu in the alkaline soil sample (**a**) and in the acidic soil samples (**b**).

Table 3. Langmuir isotherm absorption parameters for Zn and Pb and for Cu and Cd during bimetallic systems of both studied soils.

		q_{max} (mg kg^{-1})	K_L (L kg^{-1})	R^2
Alkaline soil	Zn (Pb)	666.7	0.145	0.9904
	Pb (Zn)	1000	0.118	0.8788
Acidic soil	Zn (Pb)	526.3	0.096	0.9510
	Pb (Zn)	625	0.078	0.9980
Alkaline soil	Cu (Cd)	526.3	0.23	0.9931
	Cd (Cu)	666.7	0.20	0.9869
Acidic soil	Cu (Cd)	434.8	0.09	0.9128
	Cd (Cu)	454.6	0.12	0.9913

The adsorption of all four elements in the bimetallic systems was significantly greater in the alkaline soil than in the acidic one. Specifically, the adsorption of Pb in the presence of Zn was higher (Figure 6a) than the amount retained by the alkaline soil when a solution of Pb without Zn was added (Figure 3). Furthermore, in the Cu–Cd bimetallic system, the amount of Cd bound in the alkaline soil was greater than that retained in the single-element experiment. Thus, the more toxic metals Pb and Cd are more strongly retained in the presence of the less toxic elements Zn and Cu, respectively. Similar phenomena were observed in cases of simultaneous adsorption of more than one metal on solid soil surfaces [19].

Adsorption of metal cations from the solid soil surface is due to the attractive forces that develop between the negative charge of the clay minerals and the positive charge of the metal ions [3]. Ion exchange reactions and the chemical equilibrium presented in the two-phase chemical system often describe the distribution of ions between the adsorbed amount of the metal and the amount remaining in the soil solution [8,18]. In the present study, the initial total and available concentration of metal elements may change the degree of retention of each metal in both acidic and alkaline soils. However, the soil reaction seems to be decisive for the retention of the most toxic elements in the study area. The fact that the soils were already contaminated, i.e., the metals under study coexisted at the same time, created competitive adsorption conditions [43]. The cation exchange capacity of alkaline soil (Table 1) is greater than that of acidic soil. The cation adsorption sites on the solid surface are, therefore, more in the case of alkaline soil. It has emerged from several scientific studies about the competitive adsorption of metals that the retention of lead and cadmium increases in the presence of other metals, such as copper and zinc [31,32,44].

The competition of the metallic elements to cover the available adsorption sites on the solid surface of the alkaline soil led to enhanced retention of lead and cadmium. Further experiments with multi-element metal solutions are necessary to thoroughly examine the metal concentrations that determine the maximum contaminant retention by soils.

4. Conclusions

The adsorption of zinc, lead, copper, and cadmium was satisfactorily described using both the Freundlich and Langmuir methods in the two contaminated soil samples, with a slight predominance of the Langmuir isotherm for each metal in both alkaline and acidic soil.

In the alkaline soil, a greater amount of cadmium was adsorbed. The adsorption of metals in acidic soil followed the same order, as cadmium appears to be more strongly held and bound by the same solid surface than copper (Cd > Cu). The Langmuir isotherm model described satisfactory Zn and Pb adsorption in the soil samples studied. By generating adsorption isotherms for each metal, the R^2 in all cases was quite close to unity. Additionally, the maximum amount of heavy metals that can be adsorbed (q_{max}) was calculated for both soil samples with the Langmuir model. The amount of Pb retained in the alkaline soil was greater than that of Zn. Calculating the difference between the coefficients expressing the intensity of metal adsorption for alkaline and acidic soil, it was found that the intensity of adsorption on the solid surface of the soil samples came in the following order Pb > Cu > Cd > Zn. Therefore, the effect of soil pH is greater with more harmful metals such as Pb and Cd than the less toxic Cu and Zn.

The majority of soils in moderately polluted urban environments in Greece and worldwide are alkaline. In alkaline soils, the retention capacity is greater, and, therefore, the control of the availability of dangerous toxic elements is greater. As the mass of the metallic pollutant retained by the solid surface of the soil is particularly large, metal adsorption is probably a way for soil pollution reduction. Further experiments that include a combination of metals and the study of multi-element adsorption in soils are necessary, and it would be useful to carry them out in the future.

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