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Zn (II) AND Pb (II) ADSORPTION ON TO AGRICULTURAL SOILS FROM EAST OF ALGERIA

Smail Merzougui, Youcef Mahdi, Ahmed Reda Yeddou, Boubekeur Nadjemi*

Address(es): Smail Merzougui,
Laboratoire d'Etude et de Développement des Techniques de Traitement et d'Epuration des Eaux et de Gestion Environnementale (LEDTEGE), ENS–Kouba, PB 92, 16038 Algiers, Algeria.

*Corresponding author: merzougui.chimie34@gmail.com

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ABSTRACT

Soil properties have an important role in the movement of minerals in the environment. Therefore, the study of mineral adsorption and soil properties can help solve environmental pollution problems. In the present work, batch adsorption of zinc and lead was studied on some Algerian soils (clay soil, sandy loam soil, and sandy soil), as a function of contact time, pH, metal concentration and physicochemical properties.

The results showed the metal adsorption amount depends on soil pH and initial ion concentration, soil type, temperature, exchange capacity, and metal hydrolysis. Ionic strength and organic matter content investigation indicate that, clay soil presents greater adsorption of both metals than the two other soils. The metal ions' adsorption decreases with decreasing pH and increasing ionic strength. The results showed that the adsorption amount of lead is better than that of zinc in all studied samples. The equilibrium data good fit well with Langmuir and Freundlich's models. The tested kinetic models showed that soil adsorption of these metals are biphasic and diffusion-controlled process. For all pH values, the adsorption was relatively fast at the beginning followed by a slower phase at reaching the equilibrium time.

Keywords: Agricultural soil, pollution, zinc, lead, adsorption

INTRODUCTION

Soil plays a crucial role in all terrestrial ecosystems as a fundamental component **(Bradl, 2005)**. Agricultural soils are exposed to potentially harmful substances such as heavy metals, industrial chemicals and pesticides due to the proliferation of industrial waste, mining activities, landfills, leakage from hazardous waste storage sites, and the use of wastewater for irrigation. These substances cause a global environmental health problem. The capacity of soils to adsorb metal ions from water-based solutions is of particular significance and has implications for various aspects including agricultural concerns like soil fertility, as well as environmental matters such as the remediation of contaminated soils and waste disposal. Environmental pollution is generally defined as the addition of substances that differ from the environmental components or the accumulation of natural components at levels exceeding the permissible concentrations. However, many heavy metals, such as Cu, Pb and Zn, are essential for plant and animal growth but, they can be toxic in high concentrations. This is the case of the watering process with industrial wastewater of agricultural ground when, contains some heavy metal ions like Zn, Cu, Ni, Cr and Co (Gadd, 2009). Heavy metals are the main pollutants in wastewater and even treated wastewater **(Kazemipour *et al*., 2008)**. The excessive presence of these elements in the soil can have severe consequences on the surrounding ecosystems, groundwater, agricultural productivity and human health **(Adriano, 2001)**, because they are not biodegradable, and they tend to accumulate in living creatures. Adsorption plays a critical role in the accumulation of heavy metals, making the study of adsorption processes essential for comprehending the transfer of heavy metals from a liquid phase to the surface of a solid phase **(Bradl, 2004)**. Within soil systems, heavy metals can undergo specific or non-specific adsorption reactions. The key components of soil, such as iron oxides and organic matter, play a significant role in retaining heavy metals. The adsorption and speciation of heavy metals in soils are influenced by factors such as pH, cation exchange capacity (CEC), and the presence of competing ions. Total metal concentrations in the soil are extensively dependent on soil organic carbon. Where, soil organic matter possesses a diverse range of functional groups and high cation exchange capacity (CEC), resulting in an enhanced ability to retain heavy metals primarily through surface complexation, ion exchange, and surface precipitation (**Kalbitz et al., 1998**). Generally, fine-grained soils exhibit a higher propensity for heavy metal adsorption compared to coarse-grained soils. The fine-grained fraction of soil consists of particles with a larger surface area and higher surface reactivity, along with crystalline and amorphous oxides of elements such as Fe, Mn, and Al. The number of negatively charged surface sites increases with an elevation in pH. Typically, heavy metal adsorption is minimal at low pH values **(Jung, 2008; Huang et al., 2014)**.

The Mobility and environmental fate of heavy metals in soil are reliant on their distribution coefficients (K_d) between soil and its solution, which indicate the soil's ability to retain the concerned ion, metals movement, retention, and desorption. It is affected by: the total concentration and chemical properties of metal, binding state, environmental factors, soil physicochemical characteristics (including pH and ionic strength of its solution), the simultaneous presence of competing metals, OM content, amount and type of predominant clay, and others **(Hooda, 2010; Van Herwijnen et al., 2007; Lu et al., 2015)**. Distribution coefficients (K_d) represent the soil's capacity to retain a solute and its degree of mobility in the solution phase. K_d is calculated as the ratio of milligrams of solute in the solid phase per gram of solids to milligrams of solute in the solution per milliliter of solution, with the resulting units expressed as (mL.g^{-1}). The determination of the K_d values are obtained from the tests of the adsorption isotherms **(Reddy *et al.*, 1986)**.

The adsorption of heavy metal ions (Pb and Zn) on soils has been studied extensively**. Harter *et al*. (1983)** studied Pb, Cu, Ni, and Zn adsorption on soils and the effect of pH. The results indicate the amounts of Pb, Cu, Zn, or Ni that can be retained by any soil are strongly influenced by the soil pH. The amount of adsorbed zinc in calcareous soils is higher than in soils amended with organic fertilizers **(Motaghian *et al.*, 2017)**. The organic matter content and cation exchange capacity (CEC) of the soils are important factors controlling the adsorption and desorption of Cu(II) and Pb(II). Where, the formation of the complexes metal-OM could increase the stability of the heavy metals in the soils **(Ma et al., 2010)**. The adsorption of Pb ions is greatly influenced by the pH, particularly in relation to the presence of soil organic matter (SOM). Within the neutral pH range, a higher concentration of SOM leads to an increased amount of dissolved organic matter (DOM), which in turn promotes the formation of organo-Pb(II) complexes. As a result, the solubility of Pb ions is increased **(Pincovschi *et al.*, 2017)**. Usually, experimental models are applied to represent the adsorption data. The widely used models to describe the heavy metals' adsorption onto soil and on its components are Freundlich and Langmuir isotherms.

In Algeria, the adsorption of lead and zinc is investigated in Amizor soils, and the results showed that the amount of adsorbed lead and zinc increased with the increase of pH and initial concentration, whereas the higher ionic strength decreased the adsorption capacity **(Mouni *et al.*, 2009)**.

Anthropogenic industrial and agricultural activities are the primary sources of heavy metal pollutants in the environment. These pollutants can infiltrate the soil through various means, including atmospheric sedimentation, wastewater irrigation, and contamination of the soil with heavy metals like cadmium, lead, chromium, copper, zinc, and others. While heavy metals do occur naturally in the soil, their presence is exacerbated by human activities. In Annaba (Algeria), the concentrations of cadmium, chromium, copper, lead, and zinc were found in the soil samples adjacent to the metal smelter plant, the soil of an urban area with traffic congestion, and agricultural soil with intensive agricultural activities. The results varied as lead contamination was detected in the city's soil, Cd and Cr concentrations showed one abnormally high value, while zinc never exceeded regulatory limits over the entire sampling region **(Maas *et al*., 2010)**.

There is a growing industrial and agricultural activity in Algeria and the possibility of contamination of agricultural soils by heavy metals is very likely. Among the active Algerian regions are the departments of: Bordj Bou Arreridj, Oued Souf and M'sila. In M'sila, for irrigation, farmers use a large portion of water from the Al Qasab Dam which is near to town's industrial area of Bordj Bou Arreridj. Oued Souf knows an important agricultural activity, where the farmers use chemical fertilizers to raise the productive capacity of their crops. This situation alters many biological processes and physical and chemical properties that occur in soil systems. Moreover, no emphasis has been paid so far to effect of the behaviour of mineral transfer on soil quality in these farmlands.

The aim of this study is to predict the fate and more specifically the behaviour of potential soil pollutants, by studying the adsorption of some heavy metals such as lead and zinc on soil samples that could be susceptible to metal contamination, as well as studying the effect of the most important factors in adsorption. Among them are: initial concentration, temperature, ionic strength, pH, and soil type. Moreover, the study seeks to describe the chemical and physical mechanisms involved in surface-heavy metal interaction. Furthermore, the quantification adsorption processes through the adsorption isotherms and the individual adsorption behaviour of heavy metals in the soil will also be considered.

MATERIAL AND METHODS

Soil analysis

To verify the ability and mechanisms of mineral adsorption, three soil samples were studied according to depth (0-30 cm) from the main soil series in eastern regions of Algeria: clay soil from Bordj Bou Arreridj (P1), sandy soil from Oued Souf (P2), and sandy loam soil from Msila (P3). These soils can be subject to contamination by heavy metals in the event of irrigation with water polluted by industrial effluents from nearby factories.

Before analysis, samples were air-dried and passed through 2 mm standard sieves. Some properties of these soils are given in Table 1. Soil particle size distribution was carried out by traditional sedimentation and hydrometer techniques, in the presence of Hexa-sodium metaphosphate **(Filgueira *et al*., 2006)**. The particle size analysis of the samples is reported according to the percentages of clays, silts and sands in the textural triangle to determine the texture classes. Soil pH-H_2O was measured in a mixture of soil/water (1:2.5, W/V) using a pH scale, electric conductivity (EC), cation exchange capacity (CEC) values, calcium carbonate ($CaCO_3$) and active lime were estimated following the standard procedures of **French Association for Standardization (AFNOR), (1987)**: X31-103, X31-113, X31-105, X31-106, and X31-108, respectively. Nitrogen (N) was determined by the Kjeldahl method **(Bremner, 1960)**. Soil organic matter (OM) was evaluated using the Walkley-Black wet oxidation method **(Francisco *et al*., 2009; Naelson *et al*., 1996)**. Phosphorous content was determined by the Olsen method **(Irving *et al*., 1990; Watanabe, 1965)**. Total Iron (Fe) contents were determined by the colorimetric method in the presence of phenanthroline. Total Potassium (K) and sodium (Na) were estimated by flame photometry (Eppendorf flame photometer) **(Knudsen *et al*., 1983)**. Zinc and lead concentrations were evaluated by diphenylthiocarbazone (dithizone) **(Khan *et al*., 2007; McNary, 1954)**. Each experiment was repeated three times.

Sequential extraction

To find out the distribution and mobility of zinc and lead in soil samples, sequential extraction was performed, which determines the nature of mineral binding to different soil fractions following the protocols of **Tessier *et al*. (1979), Li *et al*. (1995)** and **Mouni *et al*. (2009)**. After adsorption for 24 hours at 26 °C, many steps were performed: Step (1), exchangeable (continuous agitation for 1 hr at room temperature with 1 mol $MgCl_2$ at pH 7 or with 1 mol Na OAc pH 8.2); Step (2), Carbonate bound (Continuous stirring at room temperature with 1 mol NaOAc pH 5.0 by acetic acid for 5 hr); Step (3), Bound to Iron and Manganese Oxides (was extracted with 20 mL, 0.04 mol NH_2OH*HCl in 25% (v/v) HOAc for 6 hr); Step (4), Bound to Organic Matter and sulfide bound (Continuous agitation with 3.2 mol NH4OAc in 20% (v/v) dilute HNO3 to 20 mL for 30 min); Step (5), The residual fraction was performed with strong acids (HF, HCl, $HClO_4$). The result of each extract from the supernatant was separated by centrifugation, filtered through a 0.45 µm filter, and then analyzed.

Adsorption processes

Adsorption processes were carried out in 250 mL Erlenmeyer flasks, with a suspension of 0.5 g for clay soil (P1) and 2 g for sandy soil (P2) and sandy loamy soil (P3) in 100 mL of 0.1 M potassium nitrate containing the desired concentration of ionic adsorbates (Pb, Zn). The flasks were covered and shaken for 24 hours. Adjustments of pH were made using small amounts of potassium hydroxide or nitric acid which did not change the total volume significantly. Drops (2-3) of toluene were added to stop any bacterial activity. Metal initial concentration, from 10 to 100 mg/L for zinc and 25 to 400 mg/L for lead, was selected to obtain the equilibrium isotherm, close to the metal concentration range usually found in polluted soils. Residual zinc and lead concentrations were determined in the filtered adsorption solutions by the colorimetric method in presence of the dithizone at a specific pH. The absorption is measured at 520 nm with a device spectrophotometer UV optizen pop.

The total amount of metals retained in soil samples was obtained by the following mass balance equations:

$$\%\ \text{of removal} = \left[\frac{C_0 - C_e}{C_0}\right] \times 100\ \% \quad \text{Eq. (1)}$$

$$q_e = \left[\frac{C_0 - C_e}{W}\right] \times V \qquad \text{Eq. (2)}$$

$$q_t = \left[\frac{C_0 - C_t}{W}\right] \times V \qquad \text{Eq. (3)}$$

where, q_t is the adsorbed amount of zinc or lead per gram of soil (mg/g soil) at moment t; q_e (mg/g soil) is the capacity of soil adsorption in the solution at equilibrium; C_0, C_e and C_t (mg/L) are metal ions concentration in the solution at t0, t and equilibrium, respectively; W(g) is the air-dried mass of soil and V(L) is the volume of the used solution.

Adsorption isotherm models

The adsorption isotherm describes the correlation between the quantity adsorbed per unit weight of a solid sorbent and the amount of solute that remains in the solution at equilibrium. To analyze the equilibrium adsorption data, the Langmuir and Freundlich isotherm models were employed. These models have demonstrated their appropriateness in describing the adsorption of metal ions by various materials (**Perić *et al*., 2004**).

Langmuir model:
The Langmuir equation is the most widely equation, commonly expressed as:

$$\frac{C_e}{q_e} = \frac{1}{b\, q_0} + \frac{1}{q_0} C_e \text{ with } q_e = K_d C_e \quad \text{Eq. (4)}$$

K_d is the distribution coefficient (L/g) that represents the affinity of the metal for the adsorbent. C_e (mg/L) is the equilibrium concentration of solute, q_e (mg/g of soil) is the amount of solute adsorbed per unit weight of adsorbent at equilibrium, q0 (mg/g) is the maximum adsorption capacity or monolayer capacity, and b (L/mg) is a coefficient that relates to the relative rates of sorption/desorption at equilibrium. It is also known as the bonding energy coefficient **(Kinndiburgh, 1986)**.

Freundlich model:
The empirical equation known as the Freundlich isotherm has been found to be suitable for low concentrations of adsorbates. The Freundlich isotherm model can be represented in the following linear form:

$$\text{Log}\, q_e = \text{Log}\, K_F + \frac{1}{n} \log C_e \quad \text{Eq. (5)}$$

K_F and n are positive constants, with 1/n being the adsorption rank of Freundlich and n being only between 0 and 1. For n = 1, yields a linear-type isothermal. K_F (the Freundlich distribution coefficient) is associated with the overall adsorption capacity of the solid. This model represents an ideal case that does not account for the possible saturation of adsorption sites.**(Nagajyoti *et al*., 2010; Bradl, 2004)**.

Adsorption kinetic models

Kinetic models (first and second orders) of the adsorption of lead and zinc onto soils were studied. On the other hand, the intra-particle diffusion model was verified using the experimental data.

Pseudo-first order model:
For this model, Lagergren proposed the following equation:

$$\text{Log}\,(q_e - q_t) = \text{Log}\, q_e - \frac{K_1 t}{2.303} \quad \text{Eq. (6)}$$

where, K_1 (1/min) is the velocity constant of the pseudo- first order kinetic model.

Pseudo-second order model:
The integral form of this model is described by equation (7):

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{t}{q_e} \quad \text{Eq. (7)}$$

where, K_2 (g min^{-1}/mg) is the velocity constant of the pseudo-second order kinetic model.

Intra-particle diffusion model:
An intra-particle diffusion kinetic model is proposed by Weber and Morris to determine the rate-controlling during the adsorption process **(Mi *et al*., 2012)**. This model is important for liquid - solid adsorption. The theoretical relationship of this model is given by equation (8):

$$q_t = K_p t^{1/2} + A \quad \text{Eq. (8)}$$

where, K_p is the rate constant of the molecular diffusion model (mg/g min$^{1/2}$), The values of A provide insights into the thickness of the boundary layer.

Thermodynamic studies

To assess the thermodynamic aspects of adsorption, the Gibbs free energy (ΔG°), the entropy (ΔS°), and the enthalpy (ΔH°) were calculated from the experimental data obtained. ΔG° serves as a fundamental indicator to determine the spontaneity of a process. at a given temperature, when ΔG° possesses a negative value a phenomenon is considered to be spontaneous. Additionally, if ΔH° is positive, the process is considered endothermic, whereas a negative value suggests an exothermic process. The determination of ΔH° and ΔS° involved considering the relationship between the adsorption equilibrium constant (K_d) and Gibbs free energy at various temperatures:

$$\text{Ln } K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R}\frac{1}{T} \quad \text{Eq. (9)}$$

where, R is the universal gas constant, 8.314 J/mol K, T is absolute temperature (K), ΔS^0 is standard entropy change (J/mol K), and ΔH_0 is standard enthalpy (J/mol).
A plot of the LnKd graph as a function of 1/T, gives a linear relationship (Fig. 5). The values ΔH°/R and ΔS°/R, were determined from slope and intercept plots. Then ΔG° at any temperature is obtained from the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (10)$$

where, ΔG^0 is Gibbs free energy (J/mol).

RESULTS AND DISCUSSION

Soil properties

The particle size proportions of the soil samples were different (Tab1). The mean contents of sand, silt and clay in the samples of P1 were 63.24, 22.07 and 14.7 %, respectively. They were different from obtained values of P3 samples (89.79, 7.14 and 3.06 %) and P2 samples (96.0, 2.0 and 2.0 %). So, samples of P1 soil have a finer texture. The mobility of metals in soil is significantly influenced by the soil texture. Soil texture is determined by the distribution of particle sizes, which includes the presence of fine particles such as oxides and clay. These components serve as crucial adsorption media for heavy metals in soil. In particular, clay soils have a higher capacity for retaining metals compared to sandy soils. This was shown by the adsorption results.

The cations exchange capacity (CEC) of the semi-dry medium of P1 was 16.9 meq/100g soil. It was higher than values obtained by P3 (6.25 meq/100g soil) and P2 (6 meq/100g soil) (Tab1). The presence of organic matter plays a crucial role in the ability of soil solids to retain metals. The organic matter content was in the range of 2 to 6 % for P1 and P3. However, it was absent in P2. These results can be explained by the use of fertilizers in the P1 sample and the remains of plants. For P3, the stock of organic matter in the soil may be due to the plant tissues. Phosphorous content was found to be higher in all selected samples. Potassium content in the semi-dry medium of P2 was higher than the contents in other soils (P1 and P3). The soil pH was moderate to basic as shown in Table 1.

Metal adsorption kinetics

Pseudo-first-order, pseudo-second-order, and intra-particle diffusion models have been tested to investigate the adsorption kinetics of Pb(II) and Zn(II) on the studied soil samples at selected initial concentrations, different pH, and different temperature 26, 32, 50°C. Typical plots showing the adsorption kinetics of Pb(II) and Zn(II) in Figures 1 and 2. From these curves and in all cases, the metal adsorption rate was relatively fast at the beginning due to the greater availability of binding sites on the soil fractions, in the second phase the adsorption was slower. Maximum metal removal was achieved after 2 hours. Where, lead was initially more rapidly absorbed than zinc. It can be said that the adsorption of metal ions onto soil is carried out in a two-step process: in the first one, the adsorption capacity increases as a function of time and next, in the second step, it becomes stable after reaching the equilibrium time. The final equilibrium of lead is achieved in a short relatively time (3 hours) and it takes more time (5 hours) in the case of zinc. The multiple plots of the study of the adsorption kinetics of lead and zinc on soil samples clearly show that indicates the occurrence of two diffusion stages: rapid adsorption of metal ions on the external surface is attributed to film diffusion because there is a high number of available binding sites, followed by intra-particular diffusion much slower before the equilibrium was established. This process could be also, due to the fact that adsorption occurs on two different types of binding sites on the adsorbed particles **(Mouni *et al*., 2009)**.

Table 1 Physical and physicochemical properties of soil samples

Sample		P1	P2	P3
(%) Particle size distribution	Clay %	14.7	2	3.06
	Silt %	22.07	2	7.14
	Sand %	63.24	96	89.79
Colour		10YR6/2	5YR8/2	10YR4/8
pH-H_2O		8. 0	7.4	7.8
EC (mS/ cm)		0.20	1.01	0.46
H %		2.3	0.26	0.22
$CaCO_3$%		38.36	0.41	3.90
CEC (meq/ 100 g soil)		16.9	6	6.25
OM %		2.012	0.01	0.168
N (g/ Kg soil)		0.5	0.1	0 .21
Na^+ (mg/ kg)		389.83	483.05	525.42
K^+ (mg/ kg)		420.26	470.70	437.07
[P_2O_5] (g/ Kg)		0.754	0.842	0.6
Fe (µg/ g)		26 .12	-	0.0975

EC: Electric conductivity, measured by LF 538 WTW conductimeter.

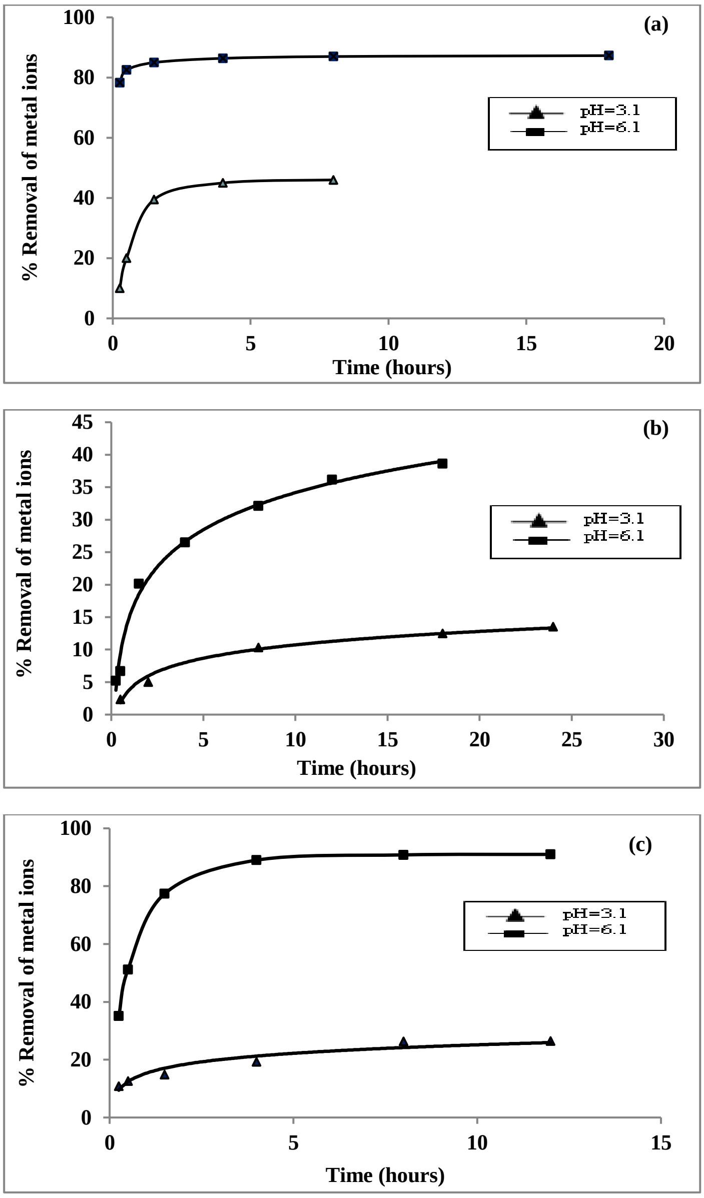


Figure 1 Effect of contact time on % removal of Zn at 26 °C [initial Zn(II) concentration, 40 mg/L ; I=0.1 M ; W/V=2/100].(a) sample soil P1, (b) sample soil P3, (c) sample soil P2.

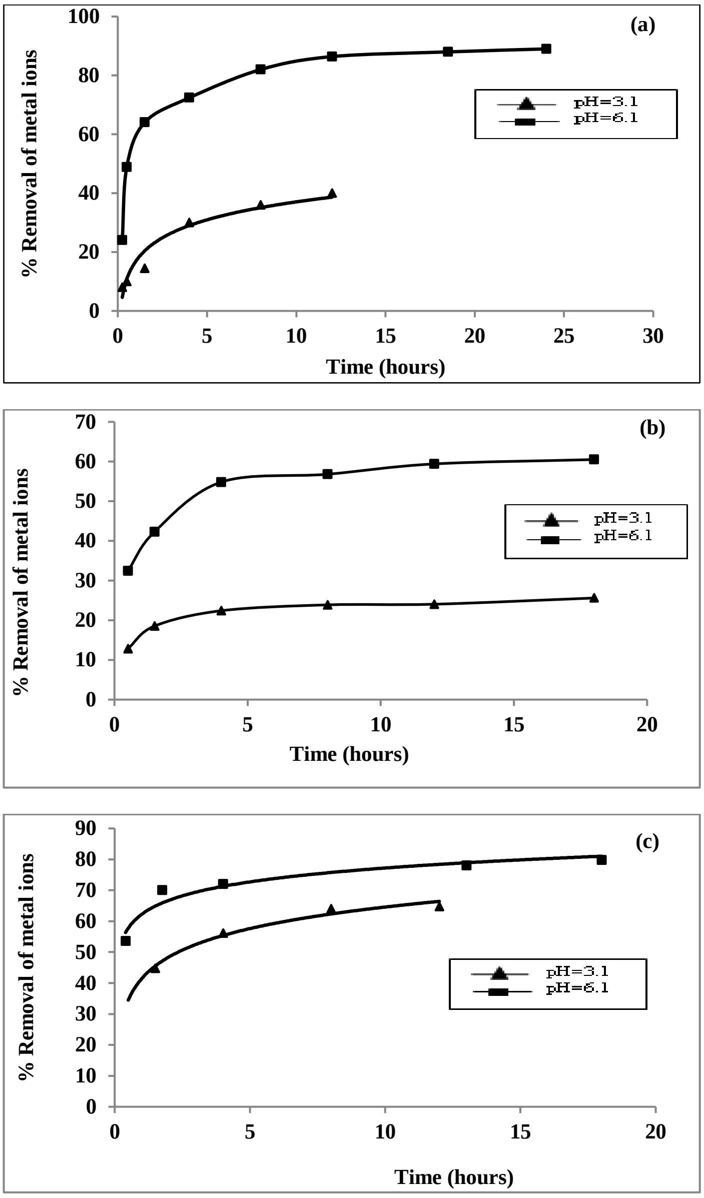
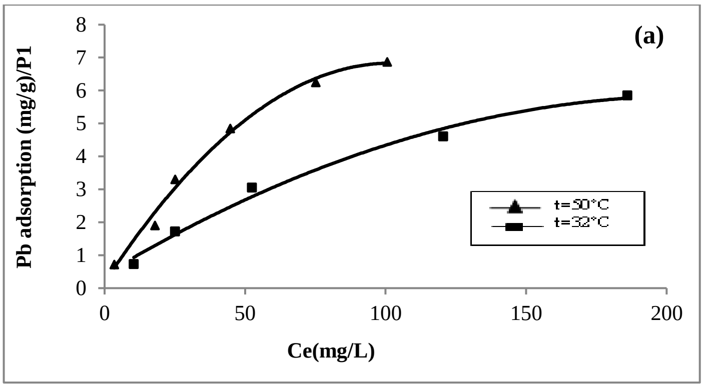


Figure 2 Effect of contact time on % removal of Pb at 26°C[initial Pb(II) concentration, 50 mg/L; I=0.1M; W/V=1/100].(a) sample soil P1, (b) sample soil P2, (c) sample soil P3.



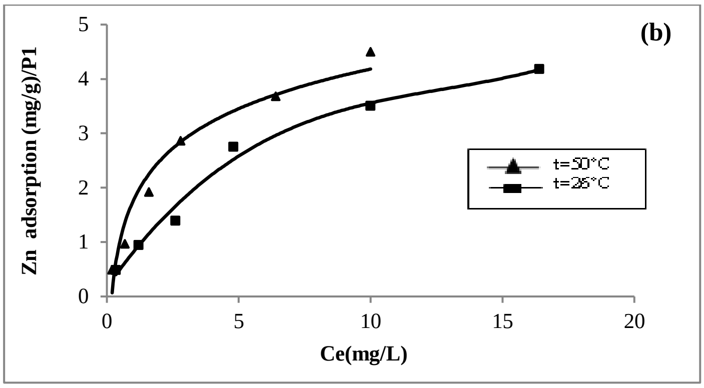


Figure 3 The adsorption of lead and zinc on the P1 soil sample at a different temperature (I=0.1M; pH = 6.1; W/V=2/100).(a) Pb-soil sample, (b) Zn- soil sample.

Influence of pH

The soil pH is a critical factor that significantly influences the properties of metal solutions and the electric charge of the soil surface. Specifically, as the pH increases, the number of negatively charged surface sites on the soil also increases. Figures 1-3 depict the adsorption outcomes for Pb(II) and Zn(II). At lower pH levels, the metal ions exist in the forms of M^{2+} and $M(OH)^+$, which results in a competitive interaction between M^{2+} and H_3O^+.

In general, the adsorption of heavy metals on soil parts increases with increasing pH. The pH is the essential parameter that determines the adsorption of cations and anions onto metal oxides **(Bradl, 2004)**. Also, the high pH can contribute to the deposition of the two metal ions as forms of $Pb(OH)_2$ and $Zn(OH)_2$.

This study it can be seen that the adsorption amount was strongly pH dependent were showed that the adsorption of Zn and Pb onto soil samples is very high at high pH and the pH has a high effect on adsorption by the soil amendments including enhanced metal adsorption through increased surface charge and this leads to metal and proton competition. On the other hand, at high pH, the metal dissolution decreased, which increases the heavy metal cations adsorption on the soil surface and when the pH value is low, metal cations faced competition with an abundance of H for available permanent charged sites, so the adsorption of heavy metal cation onto soil is limited **(Dong et al, 2009)**. Therefore, under low pH conditions, it is favorable for the release of Pb and Zn from soil to solution and increasing their migration risk to surface water and groundwater.

Influence of contact time

Time is an important factor, especially in batch adsorption processes. Sufficient time must be allowed for the complete adsorption of any substance to take place. Therefore, the adsorption characteristics are highly influenced by the mixing time between the adsorbent material and the adsorbate.

The results of the adsorption time analysis are presented in Figures 1-3. It was observed that initially, the removal efficiency of Pb(II) and Zn(II) exhibited a rapid increase with increasing adsorption time. This initial trend can be attributed to the fact that all the adsorbent sites were initially vacant, resulting in a higher concentration gradient between the adsorbate in the solution and the surface of the adsorbent. However, as time progressed, the uptake rate of heavy metal ions by the adsorbent decreased significantly. This decline can be attributed to the reduction in the number of available adsorption sites as well as the decrease in ions' concentration. Additionally, the maximum adsorption of the two metals is achieved in clay soil (P1) and sandy loam (P3) in a shorter period than the sandy soils (P2). Lead equilibrium is attained in a shorter time (2 hours) than zinc (4 hours), demonstrating higher capability of Pb(II) than Zn(II) ions for the occupation of adsorption sites in the studied soils.

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Influence of temperature

The effect of temperature on the adsorption of zinc and lead was studied at different temperatures (20-50 °C) because sunlight can warm soils up to 50°C or more. Zinc adsorption was 80 % at 32 °C and then it increased to 90 % at 50°C, while the lead adsorption increased to 94 % Fig. 3. Therefore, the temperature has a great effect on the adsorption process, where the adsorption rate increases as the temperature increases, suggesting an endothermic adsorption process. Generally, the adsorption of zinc and lead onto soils are found to be endothermic because a temperature increase aids the adsorption process through the activation of adsorption sites. It has been further confirmed by the Thermodynamic study.

Influence of ionic strength

A study showed the effect of ionic strength on the adsorption of lead and zinc by (I = 0.01 M and 0.1 M KNO3) at pH 6.1 Fig. 4. The results showed an inverse relationship, where the absorption of the heavy metals decreases with the increase of ionic strength. The effect of ionic strength increase is attributed to the competition between salt cations and metal ions on soil surface adsorption sites, the decrease of the activity coefficient ionic of lead or zinc in the presence of competing ions, and the formation of ionic pairs or chelating compounds. These results may suggest lead or zinc attraction is electrostatic and hence influenced strongly by competing ions **(Undabeytia et al., 2002; Yuan *et al*., 2007)**.

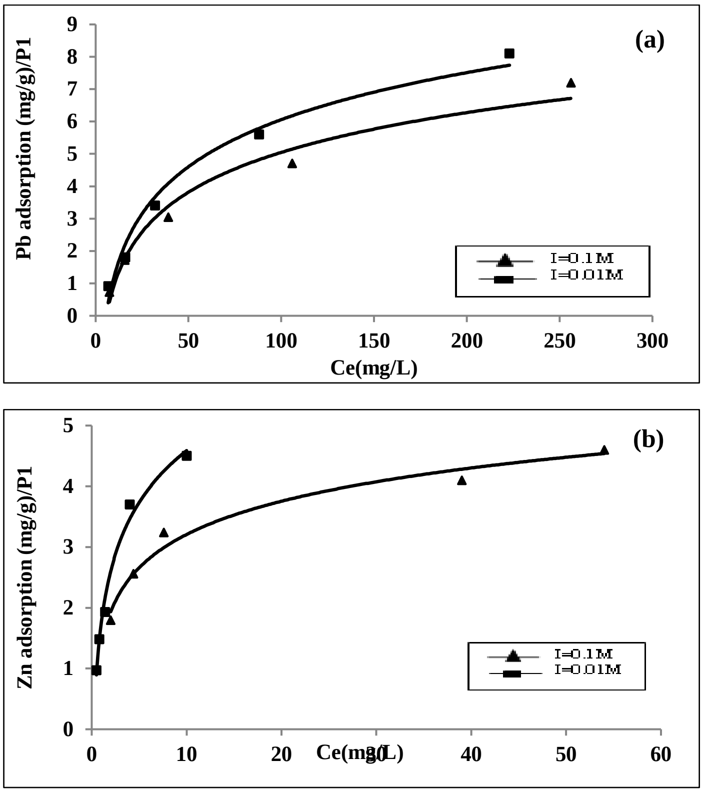

Figure 4 The adsorption of lead and zinc on the P1 soil sample at 32°C, pH = 6.1, and at different ionic strengths. (a) Pb-soil system. (b) Zn-soil system.

Role of soil type

The type of soil and composition play an important role in retaining heavy metals. In general, coarse-grained soils (P2) show fewer tendencies to retain heavy metals than fine-grained soils (P1 and P3). Fine-grained soils contain soil particles with high specific surface area, which provides high surface reaction mechanisms that presented more adsorption properties, such as clay metals, iron, manganese hydroxides, and humic acids.

Organic matter soil exhibits a large and varied number of functional groups and high CEC values. By a consequence, it leads to an increase in the retention capacity of heavy metals, mainly through surface complexation, ion exchange and surface precipitation. P1 and P3 samples content of organic matter 2.012 and 0.1677 %, respectively, have greater values than the sample P2 as shown in Table 1. This explains the higher absorption of lead and zinc in these samples. According to **Bradl *et al*. (2004)**, soil analyses by "X-ray absorption spectroscopy and ESR studies" showed that lead, copper and zinc form endophytic complexes with humic acid. Aging of soil can, also, play a significant role in heavy metal retention, as stable surface coatings form over time and the metal retention in old soils becomes very low **(Bradl, 2004)**.

Several authors have linked the increase in zinc adsorption with phosphates. This explains why the results of zinc adsorption were higher in the P1 sample **(Pérez-Novo *et al*., 2011)**. Moreover, the soil content of lime also had a considerable role in increasing the adsorption of metals, including lead, as reported by **Elkhatib *et al*. (1991)**, where in our case we obtained higher lead adsorption onto P1 soil, as it had a high lime content of 38.36 % (Tab 1).

This study showed that 4 hours of equilibrium can be sufficient for soils that contain less amounts of clay and organic carbon, while a larger period (up to 24 hours) is required for soils rich in clay and organic carbon.

Adsorption kinetics models

The results of the intra-particle diffusion model were reported in figure4 supp2 and Table 3-supp1. It can be seen that the R^2 values of lead are less than zinc results. The linear plots didn't pass through the origin, and this deviation from the origin is due to differences in the rate of mass transfer. This indicates the presence of other phenomena that affected the adsorption mechanism. The value of A for lead is higher than that of zinc, which means a greater thickness of the boundary layer during adsorption of lead.

The pseudo-second-order kinetic model obtained for the two metals lead and zinc at various concentrations showed a better correlation of result than the pseudo-first-order equation model for different adsorbents which is presented in Table 2-supp1, and Fig. 3-supp2. The correlation coefficients for second order kinetic models are greater than 0.99, and the calculated value of q_e experimental was lower than the value of q_e calculated. It was mostly found in the second-order model. Hence, the second-order model is more appropriate to explain adsorption processes in this study. q_e, the exp for lead is higher than for zinc.

Isotherm modelization

The parameters of isotherm adsorption of the Langmuir and Freundlich models resulting from the adsorption of lead and zinc ions onto soil samples were shown in Table 2, and from the correlation coefficient (R2), the obtained experimental data are well as fitting of adsorption models. The adsorbent metal is proportional to the metal in the liquid phase at a low concentration. Then, the Zn and Pb ions data reaches a peak or pseudo-peak, which can be explained by active site saturation on the surface or the simultaneous occurrence of sedimentation and adsorption. To reach the equilibrium conditions, many adsorption experiments were performed and the peak is a strong indication that this condition has been accomplished. The experiments showed the adsorption data obtained fit the Langmuir model, where the metal ions are adsorbed to form a monolayer coating on the adsorbent surface. However, the Langmuir theory cannot be exclusively applied to metal adsorption by soils since the soil surface cannot be considered uniform, but rather heterogeneous **(Jiang, 2005)**. The adsorption behavior of Zn(II) and Pb(II) on soil types is similar, except at the value of maximum adsorption capacity (q_m) of the metal ions bonded to soil fractures ranged from 0.6 to 5.6 mg/g soil for zinc and from 1.36 to 10.42 mg/g soil for lead, respectively according P2 and P3. Sample P1 exhibited a higher adsorption capacity for both metals, which can be attributed to its higher lime content **(Udo *et al*., 1970)**. The sites involved in metal absorptions are mostly probably the acidic portions of the organic matter coated on the metal phases, forming internal surface complexation **(Flogeac *et al*., 2005; Evans, 1989)**. In general, the Freundlich model also provided a reasonably good description of the equilibrium data, albeit to a lesser extent. This could be due to the heterogeneous nature of the surface locations in soil samples P1 and P3, while sample P2 exhibited a more homogeneous surface.

The adsorption of lead and zinc exhibited a significant increase with higher pH values in these experiments. The values of qm indicate that the affinity of lead and zinc in the samples is highly sensitive to changes in pH. Notably, the adsorption capacity for Pb(II) is double that for Zn(II) at the same experimental conditions. This preference for lead retention can be attributed to several factors, including electronegativity, Lewis acidity, electrical charge density, solubility, and hydrolysis constant **(Appel *et al*., 2008)**. Lead has a higher electronegativity value (2.33) compared to zinc (1.6). Additionally, the first hydrolysis constant is a reliable predictor of metal adsorption selectivity by Fe oxides and soil colloids **(Saha et al., 2002).** For the cations under investigation, the first hydrolysis constant values are 7.7 for lead and 9.0 for zinc **(Basta et al., 1992)**. Each of these factors makes Pb(II) a better candidate for To form surface - metal complex compared to Zn(II) **(Appel et al., 2008)**. It is important to note that in natural environments, adsorption phenomena are governed by numerous other parameters, and soils exhibit greater complexity. Nonetheless, our experiments provide valuable insights into the retention properties of a typical soil sample.

Table 2 Freundlich and Langmuir constants for zinc and lead adsorption on soil samples.

			Langmuir			Freundlich		
			q_m (mg/g)	b (L/g)	R^2	K_F	1/n	R^2
P1	Pb	pH=6.1	9.56	8.252	0.990	0.1587	0.7081	0.978
		pH=3.1	5.64	21.4	0.998	0.5763	0.3878	0.960
		I=0.1M	9.56	8.252	0.990	0.1587	0.7081	0.978
		I=0.01M	10.42	14.331	0.997	0.3160	0.6264	0.972
		T=32°C	9.56	8.252	0.990	0.1587	0.7081	0.978
		T=50°C	9.81	23.05	0.998	0.2839	0.7089	0.958
	Zn	pH=6.1	5.06	258.57	0.993	1.147	0.4763	0.992

Continue tab. 2

		pH=3.1	2.25	29.965	0.991	0.143	0.5593	0.982
		I=0.1M	5.06	258.57	0.993	1.147	0.4763	0.992
		I=0.01M	5.60	423.01	0.996	1.563	0.5139	0.964
		T=26°C	5.244	225.54	0.984	0.89	0.5844	0.980
		T=50°C	5.608	354.75	0.983	1.311	0.5824	0.981
P2	Pb	pH=6.1	6.075	70.372	0.993	0.973	0.4177	0.924
		pH=3.1	2.86	77.246	0.995	0.8268	0.2541	0.975
	Zn	pH=6.1	3.04	253.94	0.991	0.9714	0.301	0.866
		pH=3.1	1.042	36.25	0.994	0.0821	0.528	0.970
P3	Zn	pH=6.1	2.43	18.91	0.989	0.0730	0.711	0.989
		pH=3.1	0.60	25.62	0.979	0.0360	0.558	0.986
	Pb	pH=6.1	3.15	51.07	0.990	0.2423	0.5967	0.988
		pH=3.1	1.36	25.25	0.989	0.0640	0.6257	0.985

Adsorption thermodynamics study

The experimental results of this study are represented in Figure 5 and regrouped in Table 3. The estimated values of ΔH° and ΔS° are calculated from the matching between equation (9) and the linear equation obtained from the plot of Ln (K_d) as a function of 1/T.

Table 3 Thermodynamic parameters of adsorption of zinc and lead onto P1 soil.

	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)	ΔG^0 (KJ/mol)		
			299 K	305 K	321 K
Zn	23.5	147.997	-20.75	-21.487	-24
Pb	17.785	122.964	-18.98	-19.72	-21.686

A plot of ΔG^0 versus T was found to be linear (Fig. 6). These results in negative values of ΔG^0 at the different studied temperatures, and states that the adsorption process of Zn(II) and Pb(II) on the soil is spontaneous. The positive value of ΔH^0 means that the adsorption is endothermic; however, the positive value of ΔS^0 indicates an average random augmentation between the solid and liquid phases. Also, the decrease of ΔG^0 values with the increase of temperature indicate that a spontaneous physic-adsorption process occurred, at high temperature, which leads to a good removal of Zn(II) and Pb(II) , and this shows that the soil is a good adsorbent.

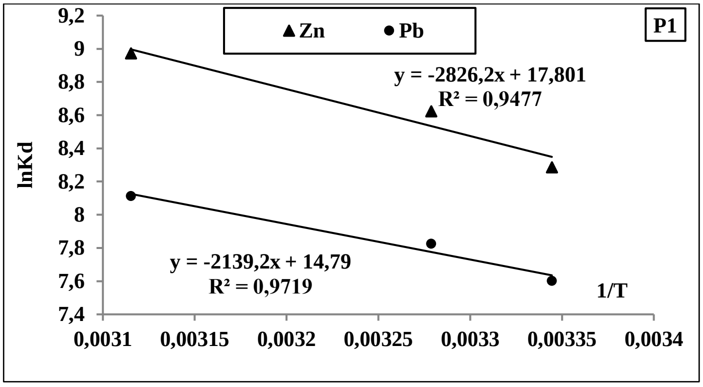

Figure 5 Plot of ln (K_d) versus reciprocal of absolute temperature, case of P1 soil (initial concentrations Zn(II), 40 mg/L and Pb(II), 50 mg/L).

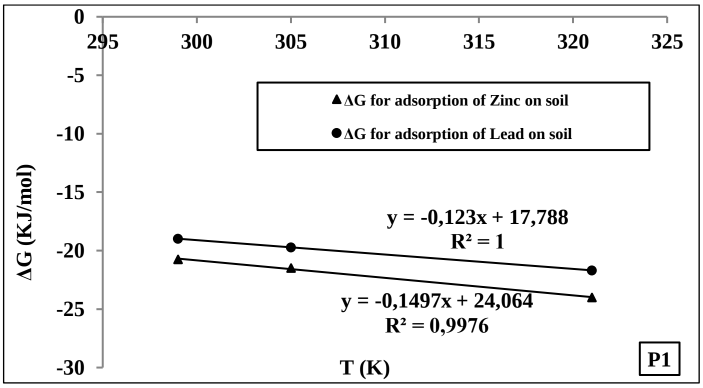

Figure 6 Plot of Gibbs free energy ΔG^0 versus absolute temperature (K) for the adsorption of Zn and Pb onto P1soil (pH 6.1; initial concentrations Zn(II), 40 mg/L and Pb(II), 50 mg/L).

Sequential extraction

From the results shown in Table 4, in the two samples P1 and P3, the proportion of zinc distribution follows the following order: extractable>exchangeable>reducible>oxidizable>residual. In sample P2, the order was: extractable>exchangeable>residual> reducible>oxidizable. The amount of active zinc the non-residual fraction in the soil represents an average of 96.3 %, and the 3.7 % remains as the stable form of zinc, which is not available for plant roots and other environmental media.

The experimental results of the series extraction procedures showed that lead was a greater percentage in the reducible fraction. The fractionation percentage of lead was as follows: extractable>reducible>oxidizable>exchangeable>residual in samples P1 and P3 and the order of exchangeable>extractable>reducible>oxidizable>residual in sample P2.

The fractional active fraction represents the predominant fraction over the remaining fraction. This correlation model did not match that described in previously studied **(Mouni et al., 2009)**.

Table 4 Results of sequential extraction (metal bonds to soil fractions %)

Fraction	Zn			Pb		
Sample	P1	P2	P3	P1	P2	P3
Exchangeble	26,66	31,65	30,74	2,85	56,51	4,41
Acid extractable	43,6	38,56	40,35	85,43	30,87	82,3
Reducible	16,74	7,13	12,52	12,21	2,21	7,71
Oxidisable	12,32	3,43	8,04	8,2	5,6	1,47
Residual	3,7	16,23	3,35	0,002	1,13	0,002

CONCLUSION

The present study showed a better understanding of the role of physical and chemical properties of soils in lead and zinc adsorption from aqueous solution. Indeed, we showed that the main factors affecting the heavy metal's adsorption were a surface factor, organic matter, lime, metal oxides and hydroxides, reaction time, pH, temperature, ionic strength and initial metal concentration. The main processes of soil retention of metal ions include the formation of multi-site complexes on the soil surface of adsorption, fixation, surface sedimentation and surface functional groups. In the three studied soils, the kinetic adsorption of zinc and lead was rapid (up to 4 hours). Moreover, the second-order model was more consistent with their absorption data.

All soil samples under the same conditions, showed a stronger affinity for Pb than Zn, while their mobility was highly dependent on pH. Heavy metal absorption is extremely important in the determination of the soil's ability to introduce pollutants into soil systems. Therefore, the higher adsorption capacities of soil sample were found to be between 5.60 and 10.41 (mg/g) at pH 6.1 respectively, and associated with higher pH, clay-silt fraction content as well as exchangeable bases, and the absorption of the heavy metals was reduced by increasing the ionic strength. The adsorption isotherms on soil samples showed agreement with Langmuir or Freundlich over a wide range of concentrations.

In studied samples, the results of sequential extraction revealed that the interchangeable phases, carbonate (extractable fraction) and Fe-Mn oxide (reducible fraction) were predominant at a pH 6.1 for both metals.

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REFERENCES

Adriano, D. C. (2001). Bioavailability of Trace Metals. Trace Elements in Terrestrial Environments, 61–89. https://doi.org/10.1007/978-0-387-21510-5_3

Appel, C., Ma, L. Q., Rhue, R. D., & Reve, W. (2008). Sequential sorption of lead and cadmium in three tropical soils. Environmental Pollution, 155(1), 132–140. https://doi.org/10.1016/j.envpol.2007.10.026

Basta, N. T., & Tabatabai, M. A. (1992). Effect of cropping systems on adsorption of metals by soils: II. Effect of pH. Soil Science, 153(3), 195-204. https://doi.org/10.1097/00010694-199204000-00010

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. Journal of Colloid and Interface Science, 277(1), 1–18. https://doi.org/10.1016/j.jcis.2004.04.005

Bradl, H. B. (2005). Chapter 1 Sources and origins of heavy metals. Interface Science and Technology, 1–27. https://doi.org/10.1016/s1573-4285(05)80020-1

Bremner, J. M. (1960). Determination of nitrogen in soil by the Kjeldahl method. The Journal of Agricultural Science, 55(1), 11–33. https://doi.org/10.1017/s0021859600021572

Daniel, E. H. (1984). Encyclopedia of library and information science, Vol. 36. Alan Kent (Ed.). New York: Marcel Dekker, 1983. Journal of the American Society for Information Science, 35(6), 373–373. https://doi.org/10.1002/asi.4630350612

Evans, L. J. (1989). Chemistry of metal retention by soils. Environmental Science & Technology, 23(9), 1046–1056. https://doi.org/10.1021/es00067a001

Dong, D., Zhao, X., Hua, X., Liu, J., & Gao, M. (2009). Investigation of the potential mobility of Pb, Cd and Cr(VI) from moderately contaminated farmland soil to groundwater in Northeast, China. Journal of Hazardous Materials, 162(2–3), 1261–1268. https://doi.org/10.1016/j.jhazmat.2008.06.032

Filgueira, R. R., Fournier, L. L., Cerisola, C. I., Gelati, P., & García, M. G. (2006). Particle-size distribution in soils: A critical study of the fractal model validation. Geoderma, 134(3–4), 327–334. https://doi.org/10.1016/j.geoderma.2006.03.008

Flogeac, K., Guillon, E., & Aplincourt, M. (2005). Adsorption of several metal ions onto a model soil sample: Equilibrium and EPR studies. Journal of Colloid and Interface Science, 286(2), 596–601. https://doi.org/10.1016/j.jcis.2005.01.027

French Association for Standardization (AFNOR). (1987). Qualité des sols, méthodes d'analyse : recueil de normes françaises, Association française de normalisation. AFNOR, Paris la défence.

Gadd, G. M. (2009). Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. Journal of Chemical Technology & Biotechnology, 84(1), 13–28. https://doi.org/10.1002/jctb.1999

Harter, R. D. (1983). Effect of Soil pH on Adsorption of Lead, Copper, Zinc, and Nickel. Soil Science Society of America Journal, 47(1), 47–51. Portico. https://doi.org/10.2136/sssaj1983.03615995004700010009x

Hooda, P. S. (2010). Introduction. Trace Elements in Soils, 1–8. https://doi.org/10.1002/9781444319477.ch1

Huang, B., Li, Z., Huang, J., Guo, L., Nie, X., Wang, Y., Zhang, Y., & Zeng, G. (2014). Adsorption characteristics of Cu and Zn onto various size fractions of aggregates from red paddy soil. Journal of Hazardous Materials, 264, 176–183. https://doi.org/10.1016/j.jhazmat.2013.10.074

Irving, G. C. J., & McLaughlin, M. J. (1990). A rapid and simple field test for phosphorus in Olsen and Bray No. 1 extracts of soil. Communications in Soil Science and Plant Analysis, 21(19–20), 2245–2255. https://doi.org/10.1080/00103629009368377

Jiang, W., Zhang, S., Shan, X., Feng, M., Zhu, Y.-G., & McLaren, R. G. (2005). Adsorption of arsenate on soils. Part 1: Laboratory batch experiments using 16 Chinese soils with different physiochemical properties. Environmental Pollution, 138(2), 278–284. https://doi.org/10.1016/j.envpol.2005.03.007

Jung, M. (2008). Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in the Vicinity of a Korean Cu-W Mine. Sensors, 8(4), 2413–2423. https://doi.org/10.3390/s8042413

Kazemipour, M., Ansari, M., Tajrobehkar, S., Majdzadeh, M., & Kermani, H. R. (2008). Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. Journal of Hazardous Materials, 150(2), 322–327. https://doi.org/10.1016/j.jhazmat.2007.04.118

Khan, H., Ahmed, M. J., & Bhanger, M. I. (2007). A Rapid Spectrophotometric Method for the Determination of Trace Level Lead Using 1,5-Diphenylthiocarbazone in Aqueous Micellar Solutions. Analytical Sciences, 23(2), 193–199. https://doi.org/10.2116/analsci.23.193

Kinniburgh, D. G. (1986). General purpose adsorption isotherms. Environmental Science & Technology, 20(9), 895–904. https://doi.org/10.1021/es00151a008

Knudsen, D., Peterson, G. A., & Pratt, P. F. (2015). Lithium, Sodium, and Potassium. Methods of Soil Analysis, 225–246. https://doi.org/10.2134/agronmonogr9.2.2ed.c13

Li, X., Coles, B. J., Ramsey, M. H., & Thornton, I. (1995). Sequential extraction of soils for multielement analysis by ICP-AES. Chemical Geology, 124(1–2), 109–123. https://doi.org/10.1016/0009-2541(95)00029-l

Lu, S., Wang, Y., Teng, Y., & Yu, X. (2015). Heavy metal pollution and ecological risk assessment of the paddy soils near a zinc-lead mining area in Hunan. Environmental Monitoring and Assessment, 187(10). https://doi.org/10.1007/s10661-015-4835-5

Ma, L., Xu, R., & Jiang, J. (2010). Adsorption and desorption of Cu(II) and Pb(II) in paddy soils cultivated for various years in the subtropical China. Journal of Environmental Sciences, 22(5), 689–695. https://doi.org/10.1016/s1001-0742(09)60164-9

Maas, S., Scheifler, R., Benslama, M., Crini, N., Lucot, E., Brahmia, Z., Benyacoub, S., & Giraudoux, P. (2010). Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environmental Pollution, 158(6), 2294–2301. https://doi.org/10.1016/j.envpol.2010.02.001

Matus, F. J., Escudey, M., Förster, J. E., Gutiérrez, M., & Chang, A. C. (2009). Is the Walkley–Black Method Suitable for Organic Carbon Determination in Chilean Volcanic Soils? Communications in Soil Science and Plant Analysis, 40(11–12), 1862–1872. https://doi.org/10.1080/00103620902896746

McNary JR, W. F. (1954). Zinc-dithizone reaction of pancreatic islets. Journal of Histochemistry & Cytochemistry, 2(3), 185-195. https://doi.org/10.1177/2.3.185

Mi, X., Huang, G., Xie, W., Wang, W., Liu, Y., & Gao, J. (2012). Preparation of graphene oxide aerogel and its adsorption for Cu2+ ions. Carbon, 50(13), 4856–4864. https://doi.org/10.1016/j.carbon.2012.06.013

Motaghian, H. R., & Hosseinpur, A. R. (2017). The Effects of Cow Manure and Vermicompost on Availability and Desorption Characteristics of Zinc in a Loamy Calcareous Soil. Communications in Soil Science and Plant Analysis, 48(18), 2126–2136. https://doi.org/10.1080/00103624.2017.1407430

Mouni, L., Merabet, D., Robert, D., & Bouzaza, A. (2009). Batch studies for the investigation of the sorption of the heavy metals Pb2+ and Zn2+ onto Amizour soil (Algeria). Geoderma, 154(1–2), 30–35. https://doi.org/10.1016/j.geoderma.2009.09.007

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a review. Environmental Chemistry Letters, 8(3), 199–216. https://doi.org/10.1007/s10311-010-0297-8

Nelson, D. W., & Sommers, L. E. (2018). Total Carbon, Organic Carbon, and Organic Matter. Methods of Soil Analysis, 961–1010. https://doi.org/10.2136/sssabookser5.3.c34

Pérez-Novo, C., Bermúdez-Couso, A., López-Periago, E., Fernández-Calviño, D., & Arias-Estévez, M. (2011). Zinc adsorption in acid soils. Geoderma, 162(3–4), 358–364. https://doi.org/10.1016/j.geoderma.2011.03.008

Perić, J., Trgo, M., & Vukojević Medvidović, N. (2004). Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. Water Research, 38(7), 1893–1899. https://doi.org/10.1016/j.watres.2003.12.035

Pincovschi, I., Neacsu, N., & Modrogan, C. (2017). The Adsorbtion of Lead, Copper, Chrome and Nickel Ions from Waste Waters in Agricultural Argilaceous Soils. Revista de Chimie, 68(4), 635–638. https://doi.org/10.37358/rc.17.4.5520

Reddy, M. R., & Dunn, S. J. (1986). Distribution coefficients for nickel and zinc in soils. Environmental Pollution Series B, Chemical and Physical, 11(4), 303–313. https://doi.org/10.1016/0143-148x(86)90047-9

Roy, W. R. (1995). Environmental Chemistry of Soils. Journal of Environmental Quality, 24(1), 199–200. Portico. https://doi.org/10.2134/jeq1995.00472425002400010029x

Saha, U. K., Taniguchi, S., & Sakurai, K. (2002). Simultaneous Adsorption of Cadmium, Zinc, and Lead on Hydroxyaluminum- and Hydroxyaluminosilicate-Montmorillonite Complexes. Soil Science Society of America Journal, 66(1), 117–128. Portico. https://doi.org/10.2136/sssaj2002.1170

Shaheen, S. M., & Rinklebe, J. (2014). Geochemical fractions of chromium, copper, and zinc and their vertical distribution in floodplain soil profiles along the Central Elbe River, Germany. Geoderma, 228–229, 142–159. https://doi.org/10.1016/j.geoderma.2013.10.012

Shugart, L. R. (2007). Principles of Ecotoxicology, Third Edition by C. H. Walker, S. P. Hopkin, R. M. Sibly, D. B. Peakall. Ecotoxicology, 16(6), 483–483. https://doi.org/10.1007/s10646-007-0151-3

Soares, M. A. R., Quina, M. J., & Quinta-Ferreira, R. M. (2015). Immobilisation of lead and zinc in contaminated soil using compost derived from industrial eggshell. Journal of Environmental Management, 164, 137–145. https://doi.org/10.1016/j.jenvman.2015.08.042

Silveira, M. L. A., Alleoni, L. R. F., & Guilherme, L. R. G. (2003). Biosolids and heavy metals in soils. Scientia Agricola, 60(4), 793–806. https://doi.org/10.1590/s0103-90162003000400029

Stögbauer, A., Strauss, H., Arndt, J., Marek, V., Einsiedl, F., & Geldern, R. van. (2008). Rivers of North-Rhine Westphalia revisited: Tracing changes in river chemistry. Applied Geochemistry, 23(12), 3290–3304. https://doi.org/10.1016/j.apgeochem.2008.06.030

Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry, 51(7), 844–851. https://doi.org/10.1021/ac50043a017

Udo, E. J., Bohn, H. L., & Tucker, T. C. (1970). Zinc Adsorption by Calcareous Soils. Soil Science Society of America Journal, 34(3), 405–407. Portico. https://doi.org/10.2136/sssaj1970.03615995003400030018x

Undabeytia, T., Nir, S., Rytwo, G., Serban, C., Morillo, E., & Maqueda, C. (2002). Modeling Adsorption−Desorption Processes of Cu on Edge and Planar Sites of Montmorillonite. Environmental Science & Technology, 36(12), 2677–2683. https://doi.org/10.1021/es011154x

Van Herwijnen, R., Laverye, T., Poole, J., Hodson, M. E., & Hutchings, T. R. (2007). The effect of organic materials on the mobility and toxicity of metals in contaminated soils. Applied Geochemistry, 22(11), 2422–2434. https://doi.org/10.1016/j.apgeochem.2007.06.013

Watanabe, F. S., & Olsen, S. R. (1965). Test of an Ascorbic Acid Method for Determining Phosphorus in Water and NaHCO3 Extracts from Soil. Soil Science Society of America Journal, 29(6), 677–678. Portico. https://doi.org/10.2136/sssaj1965.03615995002900060025x

Yuan, S., Xi, Z., Jiang, Y., Wan, J., Wu, C., Zheng, Z., & Lu, X. (2007). Desorption of copper and cadmium from soils enhanced by organic acids. Chemosphere, 68(7), 1289–1297. https://doi.org/10.1016/j.chemosphere.2007.01.046