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Batch studies for the investigation of the sorption of the heavy metals Pb^{2+} and Zn^{2+} onto Amizour soil (Algeria)

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1. Introduction

Contamination of soils with heavy metals results from several activities, including mining, smelting and metal treatment operations, vehicle emissions, deposition or leakage of industrial wastes. This pollution can pose a serious threat to plants, animals and even human beings because of bioaccumulation, non-biodegradable properties and toxicity of the contaminants even at low concentrations (Trivedi and Axe, 2000; Dong et al., 2003). Two of the most potentially toxic heavy metals are lead and zinc. They are classified as soluble and strongly hydrating cations (McBride, 1994). Since these metals are nonbiodegradable, their pollution is long lasting and would entail pollution remediation strategies in the future (Meers et al., 2005; Luo et al., 2005; Lim et al., 2005). These metals are significantly toxic (Zabetoglou et al., 2003; Petänen and Romantschuk, 2003) even in very small amounts and can also cause debilitating diseases in humans and animals as they cause irreversible changes in the body especially in the central nervous system leading to psychotic disorders and other ailments (Lewis et al., 1992; Coen et al., 2001; Dolk and Vrijheid, 2003; Järup, 2003). The metals adsorption-desorption process in both natural soils and different minerals plays a significant role in controlling the aqueous concentration of heavy metal species in soils. Heavy metal adsorption is usually described in terms of two basic

ABSTRACT

Soils play an important role in the control of metallic cations in the environment. Therefore, knowledge of the adsorption properties of soil is crucial in understanding and solving pollution problems. The aim of this paper is to study lead and zinc adsorption, onto an Algerian soil sample, as a function of the reaction time, pH, ionic strength and metal concentration. The adsorption of lead and zinc onto soil was investigated on batch equilibrium adsorption experiments. Results show that the amount of lead and zinc adsorbed increases with increasing pH and initial concentration. For pH, this increase is due to the change of the surface charge and to the hydrolysis of the adsorbing metals. The high ionic strength reduces the adsorption capacity. The competition with electrolyte and the decrease of metal activities can explain this behaviour. The adsorption isotherms allow the determination of the affinity order of metals for the surface of the soil sample as such: $Zn^{2+} < Pb^{2+}$. The equilibrium data fit well with Langmuir and Freundlich models.

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mechanisms, specific adsorption, e.g. surface complexation, and nonspecific adsorption such as ion exchange. The chemistry of Pb and Zn in soils is affected by three main factors: specific adsorption to various solid phases, precipitation of highly stable compounds and formation of relatively stable complexes with soil components (Strawn and Sparks, 1999; Appel and Ma, 2002). In recent years, many studies have been focused on the sorption-desorption of lead and zinc ions on different soil materials and a large number of experimental studies and modeling have been reported (Abd-Elfattah and Wada, 1981; Martínez and McBride, 1998; Sauvé et al., 2000; Trivedi et al., 2003). These works showed that soil pH, ionic strength of the soil solution and the simultaneous presence of competing metals are known to significantly affect sorption processes (Kookama and Naidu, 1998; Harter and Naidu, 2001). Often, empirical models which represent a description of adsorption data are applied. The two empirical models most frequently used to describe heavy metal adsorption in soils and on soil components are Freundlich and Langmuir isotherms. These models are often used to express laboratory sorption data if specific models are lacking. Amongst others adsorption of Cd, Cr, Cu, Co, Ni, Pb, and Zn onto clay, kaolin and various soils and sediments were modeled using Freundlich and Langmuir isotherms (Welp and Brümmer, 1999; Atanassova, 1999; Jain and Sharma, 2002; Ratasuk et al., 2003).

In the process of mining exploitation and ore concentrating, mine tailing and wastewaters are created, and dust is emitted. When mine waste contains lead and zinc, it will be liberated to the environment during acid mine drainage and it will be introduced into the ground-water systems (Martínez-Villegas et al., 2004). Amizour in Bejaia

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mineralized district is located in a belt of mines that occur in a semiarid region (north-east Algeria). Because of the future presence of mining waste, the Amizour soils can possibly be acidified causing, at the same time, the modification of several physical, chemical, and biological processes occurring in soil. The objective of the present work was to determine the effects of pH, ionic strength and metal concentration on the adsorption of lead and zinc by the soil of Amizour region situated in Algeria and to evaluate the potential of these metals to migrate through this soil. The results of this study could be helpful in the prediction of the metal ion transport and to evaluate the impact of lead and zinc onto soil quality. Moreover this study can give important information concerning the behaviour of a sample of an Algerian soil. The North African and African soil properties are usually not reported in the literature.

2. Materials and methods

2.1. Soil

Approximately 20 kg of a bulk soil sample was prepared by collecting 1-2 kg of loose surface soil at depth of 0-30 cm by hand digging at 15 points brownfield site located in the Amizour region (east of Algeria). This quantity was homogenised, air dried, and sieved through ASTM (American Society of Testing Materials) standard sieves. Soil particles less than 2 mm were selected and used for adsorption studies. Soil particle size distribution was determined by the sedimentation method. Soil pH was measured with a glass electrode using a 1:1 suspension of a soil to water ratio. Soil organic matter (OM) was determined by the modified Walkley and Black method (Jackson, 1973). The specific surface area of the soil sample was measured by N_2 gas adsorption at $-196\ ^\circ C$ (Brunauer, Emmet and Teller method). The cation-exchange capacity (CEC) was determined by Ca²⁺ saturation, displacement by 1 M sodium acetate and measurement of Ca²⁺ ions by atomic spectroscopy. Total contents of Fe and Ca were determined by X-ray fluorescence spectrometry (XRF) using a Philips PW-2400 X-ray spectrophotometer with Rh and Au excitation tubes using a series of international reference geological standards. The obtained results of soil sample are given in Table 1. The metallic solutions were prepared from lead and zinc nitrates. Lead nitrate (Pb(NO₃)₂) was purchased from Panreac and zinc nitrate $(Zn(NO_3)_2, 4H_2O)$ from Merck. All solutions were prepared with demineralised water and adjusted to 0.1 M ionic strength with sodium nitrate in order to limit colloid formation and filter blocking (Radu et al., 2007). Each experiment was repeated twice to check the reproducibility.

2.1.1. Sequential extraction

Sequential extractions of soil samples following the protocol of Tessier et al. (1979) were conducted. The main purpose of a sequential extraction was to investigate the speciation of trace metals. The five operationally extraction steps were reported in detail by Delmas et al. (2002). The association of chemical elements with

Table 1

Chemical	and p	ohysical	properties	of	Amizour	soil	
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Particle size (%)	
Clay %	39.7
Silt %	20.6
Sand %	39.5
Surface area $(m^2 g^{-1})$	29.4
pH	6.9
CEC (cmol kg ^{-1})	17.8
$OM (g kg^{-1})$	1.7
Total N(g kg ⁻¹)	2.6
CaCO ₃ (%)	1.4
Fe ₂ O ₃ (%)	3.4
CaO (%)	2.6

different fractions in soil is investigated through several different dissolution steps: (i) exchangeable fraction (salt-displaceable, agitation with 1 M MgCl₂ at pH = 7 during 1 h), (ii) carbonate bound (acid extractable fraction 1 M CH₃COONa adjusted to pH = 5.0 acetic acid during 5 h), (iii) Fe/Mn oxide bound (reducible fraction, 0.04 M NH₂OH · HCl), (iv) organic matter and sulphide bound (oxidisable fraction, 30% H₂O₂, 0.02 M HNO₃, 3.2 M CH₃COONH₄ in 20% HNO₃), and (v) total extraction (residual, HNO₃, HNO₃ + HClO₄, 6 M HCl). The extracts from each step were filtered through a 0.45 µm filter, acidified and analyzed by AAS. The results of the sequential extraction procedure are reported in Table 2.

2.2. Sorption studies

Batch agitation studies were performed to evaluate the metal mobilization (Pb, Zn) from the soil as a function of pH and initial concentrations. All the experiments were carried out at constant temperature (23 °C) and ionic strength (I=0.1 M) under continuous stirring (end-over-end rotation, about 150 rpm) for a known period of time (10, 30, 60, 90, 150, 180, 300, 600 min). pH conditions were chosen in order to approach natural conditions for neutral-acid soils.

The pH was adjusted with diluted solution of NaOH or HNO₃. The initial concentration of the metal solutions was selected in order to obtain the equilibrium isotherm in a concentration interval close to metal concentrations usually found in polluted soils. Then, the solutions were centrifuged at 3900 rpm for 10 min and the supernatants were filtered through a 0.45 μ m pore size membrane. The lead and zinc concentrations spectrophotometer (Shimadzu AA6500). The isotherm study was conducted in a series of 200 ml Erlenmeyer flasks. Each flask was filled with 100 ml of different initial Pb(II) or Zn (II) concentrations and adjusted to pH 2 and 7. After equilibrium, the solution was separated and analyzed. The initial concentrations of solutions taken for the studies were 10, 20, 30, 60, and 100 mg l⁻¹. The total amount of metal retained by the solid phases was obtained by mass-balance equation:

$$q_t = \frac{(C_0 - C_t) \times V}{W} \tag{1}$$

where q_t is the amount of metal sorbed per unit mass of soil (mg g⁻¹) at a time t, C_0 and C_t (mg L⁻¹) are the initial metal concentration solution and at the time t respectively, V is the volume of the solution used (1) and W is the air dried mass of soil (g). Adsorption characteristics can be depicted by an adsorption isotherm.

The experiment isotherm data were analyzed with both the Langmuir model and the Freundlich model. The Langmuir equation has the form:

$$q_{\rm e} = q_{\rm m} \frac{bC_{\rm e}}{1 + bC_{\rm e}} \text{ with } q_{\rm e} = K_{\rm d}C_{\rm e} \tag{2}$$

where K_d is the distribution coefficient that characterizes the affinity of the metal for the sorbent. C_e is the equilibrium concentration of solute $(mg l^{-1})$, q_e is the amount of solute adsorbed per unit weight of adsorbent $(mg g^{-1} \text{ of soil})$, q_m is the maximum adsorption capacity $(mg g^{-1})$, or monolayer capacity, and b $(l mg^{-1})$ is a coefficient which reflects the relative rates of sorption and desorption at

Table	2		
Metal	bound	fractions	(%).

Fraction	Zn	Pb
Exchangeable	3.2	2.8
Acid extractable	32.3	10.8
Reducible	51.8	62.7
Oxidisable	7.1	9.6
Residual	5.6	14.1

equilibrium and is thus the bonding energy coefficient (Kinniburgh, 1986). The Freundlich sorption isotherm using the log-transformed form:

$$\log q_{\rm e} = \log K_{\rm f} + \frac{1}{n} \log C_{\rm e}.$$
(3)

This model represents an ideal situation, which does not include the possible saturation of the sorption sites (Sparks, 1995). Where K_f is the Freundlich distribution coefficient related to the total adsorption capacity of the solid, and 1/n is the Freundlich sorption exponent. The goodness-of-fit for all equations was estimated by the coefficient of determination. Statistical analysis was performed using the Excel program.

3. Results and discussion

3.1. Kinetics of metal retention

Typical plots showing the kinetics of adsorption of Pb^{2+} and Zn^{2+} at different initial concentrations (low to high) and at different pH are presented in Figs. 1 and 2. From these plots, it is found that the adsorption capacity increases with increasing contact time and becomes constant after the equilibrium time is reached. Equilibrium is attained within 2 h for lead and 4 h for zinc. These preliminary kinetic experiments strongly indicate that the adsorption of lead and zinc metal ions on soil is a two-step process: a rapid adsorption of metal ions on the external surface followed by possible slow intraparticle diffusion. This two-stage process can also be due to the fact that adsorption occurs onto



Fig. 1. Kinetics of adsorption. (a) Pb-soil system, initial Pb^{2+} , 10 mg I^{-1} ; (b) Pb-soil system, initial Pb^{2+} , 30 mg I^{-1} ; (I = 0.1 M).



Fig. 2. Kinetics of adsorption. (a) Zn-soil system, initial Zn^{2+} , 10 mg l^{-1} ; (b) Zn-soil system, initial Zn^{2+} , 30 mg l^{-1} ; (l = 0.1 M).

two different types of binding sites on the adsorbent particles. Similar results have also been obtained by other investigators (Serrano et al., 2005; Flogeac et al., 2007).

In all cases, the rate of metal adsorbed was relatively rapid in the beginning because of the greater availability of the soil sites. The maximum percent removal was attained at about 2 h and final equilibrium was reached after 5 h in all cases. Lead was initially more rapidly sorbed than Zn. For example at high concentration and at 5 h, more than 75% of the initial Pb was sorbed. In contrast, under similar conditions, Zn sorption reached 43% of the initial concentration. For practical reasons, the duration of all the experiences was fixed at 10 h.

3.2. Influence of pH

The pH plays an important role on the sorption of Pb(II) and Zn(II) (Figs. 1–3). It has been found that the maximum percent sorption of Pb (II) was observed at pH = 7 and the amount adsorbed was found to increase with increasing pH. As anticipated, the role of pH in controlling metal adsorption is demonstrated here. Such increase in adsorption can be attributed to the favourable change in surface charge and to the extent of hydrolysis of the adsorbing metal ion change with varying pH. At low pH, the metal ions are present in the form of M^{2+} and $M(OH)^+$. This leads to an effective competition between H⁺ and H₃O⁺. Aqueous speciation of lead and zinc as a function of pH was studied at 30 and 10 mg l⁻¹ of the respective metal in the nitrate form using the computer program Visual MINTEQ, Version 2.30. Below pH 8.0, Pb occurs predominantly as Pb²⁺ and Pb (OH)⁺, a nitrate species PbNO³⁺ is also

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Fig. 3. Effect of initial solution pH on the adsorption of lead and zinc into soil (a) Pb, S/L = 0.5 g/100 ml (b) Zn, 1 g/100 ml (l = 0.1 M).

present in a significant amount up to pH 6.5. After which its concentration starts decreasing. Small amounts of other Pb species $(Pb(NO_3)_2 (aq), Pb_4(OH)_4^{4+}, and Pb_2(OH)^{3+})$ also occur in solution, but their concentration does not significantly change over the entire pH range. Zinc occurs predominantly as Zn^{2+} . The concentration of Zn^{2+} starts to decrease after pH \approx 7.5 in both systems. Other Zn species $(ZnNO^{3+}, Zn (NO_3)_2(aq), Zn(OH)_3^{-}, Zn(OH)_4^{2-}, and Zn_2(OH)^{3+})$ occur at negligible concentrations under the solution conditions of our experiments.

As the surface charge becomes more negative with increasing pH, the surface attracts bivalent metal cations for adsorption. Furthermore, the proportion of hydrated ions increases with pH and these may be more strongly adsorbed than unhydrated ions. Therefore, both these effects are synergistically enhancing the amount of adsorption at higher pH (Chang et al., 1997).

3.3. Influence of ionic strength

The influence of ionic strength (I = 0, 0.03 and 0.1 M NaNO_3) on Pb and Zn adsorption by soil was investigated at pH = 7.0 (Fig. 4). A significant influence of ionic strength on the adsorption of lead and zinc was observed. The sorption of lead and zinc decreased with the increase of ionic strength. The effect of ionic strength could be ascribed to: (1) the competition of high concentrations of cations in electrolyte with lead or zinc for the adsorption sites on soil surface. An increase of ionic strength will supply more Na⁺ ions which compete with lead or zinc for the adsorbing sites on soil surface (Undabeytia et al., 2002); (2) the decrease of activities of lead or zinc due to the increase of ionic strength; (3) the formation of ionic pairs or chelating compounds (Songhu et al., 2007). Additionally, the presence of salts



Fig. 4. (a) Amount of Pb adsorbed by soil sample at pH 7 at different ionic strengths; (b) amount of Zn adsorbed by soil sample at pH 7 at different ionic strengths.

may compress the electric double layer surrounding negatively charged surfaces (Phillips et al., 2004; Xu and Zhao, 2005), which contributed to the release of adsorbed lead or zinc. The observed variations in Pb and Zn sorption with ionic strength may be explained by the formation of outer-sphere complexes since Na⁺ in the background electrolyte could compete with the metal ions adsorbed on the outer-sphere sorption sites and reduced the adsorption. Whereas Na⁺ would not have competed for the inner-sphere sites, as independence of sorption with background electrolyte concentration has been interpreted to indicate that the sorption process is primarily non-electrostatic in nature (Stumm and Morgan, 1996).

3.4. Sorption isotherm

The adsorption isotherms of metal ions onto soil sample are reported in Fig. 5. We can note that at low-concentration, the metal adsorbed is proportional to that present in the liquid phase. Then the isotherm reaches a plateau or a pseudo-plateau, which probably corresponds to the saturation of the surface or to a co-precipitation phenomenon (i.e., sorption and precipitation simultaneously). Equilibrium adsorption experiments were performed to ensure that the equilibrium conditions are reached. The presence of a plateau indicates that this condition is satisfied.

For all remaining experiments, the Langmuir isotherm produced an excellent fit for the data. From these results a number of observations can be made. The maximum amount of metal bound to soil particles can be ranged (on the plateau) from 1.79 to 7.14 mg g^{-1} and 0.835 to 1.936 mg g^{-1} for lead and zinc, respectively. The Langmuir isotherm

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Fig. 5. Sorption isotherms at 23 °C for retention of Pb and Zn, at different pH values: (a) Pb, S/L = 0.5 g/100 ml (b) Zn, 1 g/100 ml (I = 0.1 M).

parameters were deducted for each metal by performing a linear regression and are reported in Table 3. The good agreement (R^2) with the experimental data suggests that the metal ions sorbed form a monolayer coverage on the adsorbent surface. The sites involved in the metal sorption are probably the acid moieties from the organic matter coated onto the mineral phases (Flogeac et al., 2005). The Freundlich isotherm parameters are also added for comparison. Generally, to a lesser extent, the equilibrium data were also well described by the Freundlich model, probably due to the real heterogeneous nature of the soil sample surface sites.

In these experiments, lead and zinc adsorption increased markedly with pH, from $q_m = 1.79 \text{ mg g}^{-1}$ at pH=2 to $q_m = 7.14 \text{ mg g}^{-1}$ at pH=7 (lead), and from $q_m = 0.835 \text{ mg g}^{-1}$ at pH=2 to $q_m = 1.936 \text{ mg g}^{-1}$ at pH=7 (zinc).

The affinity parameter, *b* varied from 0.026 to $0.210 \,\mathrm{lmg}^{-1}$ and 0.019 to 0.124 lmg^{-1} for lead and zinc, respectively. A higher value of adsorption coefficient for lead suggested a strongest affinity with soil. Both the affinity parameter and maximum adsorption capacity ($q_{\rm m}$)

Table 3

Langmuir and Freundlich parameters for lead and zinc adsorption onto soil sample at pH 2 and 7 (23 $^\circ C).$

	рН	Isotherm						
		Linear	Langmuir			Freundlich		
		$K_{\rm d} \ ({\rm l} \ {\rm mg}^{-1})$	$q_{\rm m} ({\rm mg} {\rm g}^{-1})$	$b(l mg^{-1})$	R^2	K _f	1/n	R^2
Pb	2	16.4×10^{-3}	1.79	0.026	0.98	0.101	0.5807	0.93
	7	135.2×10^{-3}	7.14	0.210	0.99	1.717	0.382	0.92
Zn	2	6.6×10 ⁻³	0.835	0.019	0.97	0.0332	0.631	0.92
	7	27.6×10^{-3}	1.936	0.124	0.97	0.462	0.325	0.90

indicate that the lead and zinc sorption capacity of soil sample is largely perceptible to pH changes. In fact, soil retained more lead than zinc in the studied concentration range. It seems that preferential retention can be explained by three factors which are in favour of Pb, namely, electronegativity, Lewis acidity and first hydrolysis constant (McBride, 1994). The electronegativity in this case is higher for Pb (2.33) than Zn (1.6). However, the first hydrolysis constant is most predictive for metal adsorption selectivity by specimen Fe oxides and soil colloids (Saha et al., 2002). The value of the first hydrolysis constant (pK) of the cations under study is equal to 7.7 and 9.0 for lead and zinc respectively (Basta and Tabatabai, 1992). Each of these factors makes Pb a better candidate for inner-sphere surface sorption/complexation reaction compared to Zn (McBride, 1994). In natural environment, systems are more complicated because several other parameters govern the adsorption phenomena, and the natural solids are much more complex systems. But our experiments give some useful pieces of information on the retention properties of a model soil sample.

3.5. Geochemically based extractions

The percentage fractionation of zinc (Table 2) follows the order: reducible > extractible > oxidisable > residual > exchangeable. The non-residual fraction of zinc represents on the average of 94.4% which is the amount of active zinc in soils while 5.6% of the residual fraction may be considered as the stable form of zinc, which is not available to plants and other environmental media. The results of the sequential extraction procedure show that lead was predominant in the reducible fraction. The percentage fractionation of lead follows the order: reducible > residual > extractible > oxidisable > exchangeable. The part of the reducible fraction and residual fraction represents 62.7% and 14.1% respectively. This association pattern is in line with those previously described in the literature. Norrstrom and Jacks (1998) reported that lead and zinc occurred in soils mostly associated with the oxide-bound reducible fraction.

The sequential extraction results of the soil before and after sorption experiments at pH 2 and 7 are illustrated in Fig. 6a–b. The redistribution of metals in soil has been affected by pH of experiments. At pH 7, only two phases play a significant role during the sorption of zinc. The phases of the soil which intervene are the extractable and exchangeable ones (Fig. 6.a). The reducible phase intervenes in a lesser measure. The contributions of oxidisable and reducible phases do not seem to change during the sorption. Before the sorption, one of the phases retaining preferentially the zinc is the reducible phase. This last was saturated, because during the sorption experiments, the quantities of zinc fixed on oxides varied little. In fact, at pH 7, the extractible fraction is mainly requested for the retention of zinc. 52.3% of zinc retained by the soil was attributed to this fraction. On the other hand, at pH 2 the zinc contained in the extractible phase is low. At these conditions zinc is mainly retained by the exchangeable fraction.

The lead in the soil studied is strongly associated with the carbonate and Fe–Mn oxide phases (ca. 73.5%), with only a slight amount in the organic phase (ca. 9.6%) and a negligible proportion in the exchangeable phase (ca. 2.8%) (Fig. 6a). At pH 7, the participation of reducible phase is not important. This phase is supplanted by the carbonate phase (extractible) and the relative part of this phase (extractible) passes from 10.8 to 42.5%. The percentage of lead sorbed at pH 2 becomes very important. It seems that during the action of an acid solution the lead present in the extractable phase becomes less and the exchangeable one is the limiting phase.

4. Conclusion

This study allows a better understanding of the role of different physicochemical parameters in metal retention, such as reaction time, pH, ionic strength and initial metal concentration. Indeed, we showed that the metal adsorption is relatively rapid (less than 5 h).

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Fig. 6. Distribution of Pb and Zn in soil sample before and after batch sorption experiments at pH 2 and 7.

As expected, soil study has a stronger affinity for Pb than Zn when introduced to the soil at the same conditions and mobility was strongly pH dependent. The adsorption of heavy metals is very important in determining the capacity of soils to respond to the introduction of these pollutants into soil systems. The maximum amount of lead and zinc bound to soil sample was found ranging from 7.14 mg g⁻¹ to 1.936 mg g⁻¹ at pH=7, respectively and the adsorption of heavy metals was reduced by increasing ionic strength.

The sequential extraction studies revealed that carbonates (extractable fraction) and Fe–Mn oxide phases (reducible fraction) are predominant in the soil sample for the two heavy metals studied. At pH 7, the extractible fraction is mainly requested for the retention of zinc and at pH 2; zinc is mainly retained by the exchangeable fraction. At pH 7, the participation of Fe–Mn oxide phase (reducible fraction) is not an important carrier for lead. At pH 2, the exchangeable fraction becomes more important.

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