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Chemical speciation of lead adsorbed onto volcanic ashes by ICP-OES and XANES

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In this work, the potential of Volcanic Ashes (VA) from the Cameroon Volcanic Line (CVL) as adsorbents of Pb(II) from aqueous solutions was studied. The chemical speciation of lead adsorbed onto volcanic ashes based by means of inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray absorption near edge spectroscopy (XANES) study is reported. The experiments were done using the ashes from CVL to remove lead in aqueous solutions. The maximum value of the adsorption capacity of lead in VA was determined to be 7.60 mg g^{-1} at pH 5. Regarding the adsorption process, the contribution of the mixture Pb components after adsorption and a strong interaction of adsorbed Pb with the surface of volcanic ashes were proven. The chemical elements present in the VA and their concentrations are determined by ICP-OES. Chemical speciation was carried out measuring Pb saturated VA sample at the L3 edge (13035 eV) at the XAFS beam line in Elettra Sincrotrone (Trieste). The XANES measurements showed that the Pb removal occurred mainly by microprecipitation of lead acetate and carbonate associated with a possible ion-exchange forming lead monoxide.

Keywords: X-ray absorption spectroscopy; volcanic ashes; microprecipitation; ion exchange.

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1. Introduction

In general, the lands around volcanoes are frequently subjected to the intermittent flow of lava and deposition of volcanic ash (VA) during the volcano's eruption. Monthly small-scale explosive volcanic eruptions can emit more than a million cubic meters of ashes into Earth's atmosphere [1]. As soon as these ejections from volcanic eruptions are deposited onto the surrounding soils, the soil formation process starts, which produces a modification in its mineralogical composition leading the volcanic soils to have some specific properties such as water holding capacity low bulk density.

The fertile volcanic soils found in Cameroon result from the chemical weathering of volcanic rocks ejected from Mount Cameroon volcano. They possess various properties useful in diverse applications, including agriculture, construction, and wastewater treatment. Mount Cameroon is the unique active volcano along the CVL and is an important regional feature in West-Central Africa. The analysis of eruption lava showed a variation in its chemical composition up to the normal level standard of good quality of soils [2]. Despite of these results, few chemical speciation studies were carried out to contribute to the improvement for keeping safety the environment and soils of the involved localities. In addition, these authors were interested in the quality status of the neighboring soils of the Mount Cameroon volcano by identifying trace elements [2]. The results showed that water is acidic and that some metals such as Cr, Zn, Ni, and Pb have elevated concentrations resulting from the volcanic eruption. These volcanic soils are acidic and are mainly dedicated to the agricultural and water purification sectors. The physical, mechanical, and reactivity properties of VAs based on geopolymer mortars have also been evaluated [2,3]. VA from Cameroon then proved being effective for cement manufacturing and in the agricultural sector. However, these have not been tested as an adsorbent to remove contaminants in an aqueous solution. For instance, few works were dedicated to studying their use as material for the removal of arsenic (As), zinc (Zn), lead (Pb), and phosphorous (P) from aqueous solution using VA from Puyehue-(Chile), Kerman-(Iran) and Ibaraki-(Japan) [5–7]. In addition, the inhalation and ingestion of some toxic elements such as chromium (Cr), cadmium (Cd), nickel (Ni), iron (Fe), Zn, and Pb are harmful to human or animal health when they are chronically exposed since they can cause severe damages leading to dangerous diseases such as circulatory disorders, chronic bronchitis, dental and skeletal fluorosis [8]. These elements could be removed from water using VA as adsorbent material at the same level as any other adsorbent, such as the low-cost synthetic minerals [9], smectite, and kaolinite [10].

It should be noted that the removal of Pb in aqueous solutions with such VA materials is not well documented, even though its recommended concentration is 0.1 mg L^{-1} for drinking water [11]. Nonetheless, the removal of Pb^{2+} onto silicon-rich biochars was investigated by [12] using techniques such as X-ray Absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS), among others. They found that the K, Ca, Cu, Mn, and Fe elements were significantly related to Pb and were released in the samples. In addition, they showed that $Pb_3(PO_4)_2$, $PbSiO_3$, and $PbCO_3$ species were formed with similar structures to lead carboxylate.

This study focuses on the assessment of the VA materials from the Moungo zone (Fig. 1) of the Cameroon volcanic line (CVL) between the mount Cameroon volcano and Mount Koupé, for their use as natural adsorbents to remove Pb^{2+} pollutant from aqueous solutions. Fourier transform infrared (FTIR), inductively coupled plasma optical emission spectroscopy (ICP-OES), and X-ray absorption near edge structure (XANES) techniques are used to characterize the studied VA. These techniques were used in some studies to assess the whole properties of the adsorbed VA [5,6]. XANES was also utilized to probe the electronic and structural properties of a specific element in various compounds [12,13].

2. Materials and methods

The raw materials VA samples were collected in the Moungo zone inside the CVL in the center of the CIMENCAM quarry at sites 1 and 2, as indicated in Fig. 1. The details on the collected samples labelled P1, P2 and P3 are given in Table I. All collected samples were air dried for 24 h.

The adsorption tests were done using the methodology described in [14]. An unsaturated solution of 100 mg L^{-1} of Pb^{2+} solution was prepared from $Pb(NO_3)_2$ reagent grade (solubility in water 597 g L^{-1}) and deionized water. Then, 10 mL of the solution was collected to analyze the initial concentration, and then 40 mL of the same solution was mixed with 0.2 g of sample P1; the final concentration was measured at the end of the experiment. The pH of the mixture was adjusted at three values: 3, 4, and 5, respectively. The suspensions were left for 7 days to reach the equilibrium state, and their pH was adjusted daily. The raw sample and Pb^{2+} adsorbed sample were respectively named UVA (unsaturated VA) and Pb-SVA (Pb saturated VA). The Pb^{2+} initial and final concentrations were measured using flame atomic absorption spectroscopy (FAAS). The Atomic absorption spectrometer (Varian 220) was operated under the current of 5 mA at the wavelength of 261.4 nm with 0.5 nm slit width.

The ICP-OES measurements were performed by dissolving with concentrated HNO_3 and HCl the VA powder in a proportion of 0.1 g of VA in 10 mL (1:100 w/v) [15]. The equipment used was an ICP-OES brand Varian model 738 ES with the torch placed at the axial position and nebulizer flow of 0.75 L min^{-1}. All samples were analyzed in triplicate, having a relative standard deviation < 2.0 and with a limit of the detection of the apparatus below 0.01 mg kg^{-1}. The results of the average concentration of the elements in the VA samples are reported in Table II. Infrared (IR) analysis of the VA was performed on a Thermo Scientific Nicolet iS10 FTIR spectrophotometer. The analysis comprised 32 cycles in a range from 520 to 4000 cm^{-1}. The VA samples were mixed with KBr in a 1:300 ratio. A toxicity characteristic leaching procedure was designed to determine the mobility of different inorganic analytes present in solid waste (VA). This procedure was according to US EPA international method 1311 [16].

To perform XANES measurements, the pellets for VA samples were prepared by mixing 100 mg of the saturated Pb-SVA-P1 with 50 mg of polyvinylpyrrolidone. XANES measurements of Pb-SVA-P1 were done in fluorescence mode at the L3 edge of Pb, at the XAFS beamline [17] of Elettra Synchrotron (Trieste, Italy). The storage ring was operated at 2 GeV yielding a current of 310 mA. The first inflection point of the L3-edge XANES spectrum of Pb was assigned to 13,035 eV to calibrate a double crystal silicon Si (111) monochromator. The x-ray absorption data were collected in the energy range of [12,735.00$-$13,781.75] eV and the wave vector range of [0$-$14] $Å^{-1}$. All spectra collected for each sample were averaged and then normalized to one absorption spectra using ATHENA software [18]. Principal component analysis (PCA) and Target Transform (TT) were used in ATHENA [18] to determine the number and types of the standards useful of a linear combination fitting (LCF). LCF was performed in an energy range of -20 eV below to +30 eV above the edge using at least 4 model compounds according to PCA. The lead compounds, PbS, PbO, PbO_2, Pb_2O_4, $Pb(CO_3)$, $Pb(SO_4)$, $Pb(C_2H_3O_2)_2$, and Pb-sorbed onto Goethite (Pb-α-FeOOH) were utilized as standards for the fitting. The XANES spectra of all compounds were compared to the spectra of VA samples to check the oxidation state and guess the suitable standards. The R_{factor} indicates the most likely combination resulting in the best fit, which guides the choice of the good components possible present in the sample.

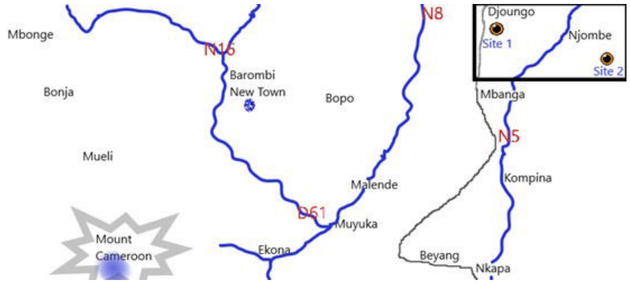

FIGURE 1. Map showing the location of sampling points. The black rectangle indicates the area where the samples were collected.

TABLE I. Description of the VA and the geographic location.

Samples	**Description**	**Colour**	**Geographic coordinates**		
	North	**East**	**Altitude**		
P1	Big scoops particles	Gray	$04^\circ35'09''$	$09^\circ37'37''$	134 ± 3 m
P2	Average particles	Gray	$04^\circ35'12''$	$09^\circ37'37''$	140 ± 3 m
P3	Small particles	Brown	$04^\circ35'33''$	$09^\circ37'32''$	147 ± 3 m

TABLE II. Concentration of trace elements in mg Kg^{-}1 in volcanic ashes for all samples obtained from ICP-OES measurements. The values correspond to the average concentration. Relative standard deviation < 2.0 %.

Elements	**P1**	**P2**	**P3**	**Elements**	**P1**	**P2**	**P3**
Al	5,739	98,782	74,825	Mg	6,883	41,975	43,995
B	29	21	25	Mn	789	1,719	1,649
Ba	188	58	163	Na	8,186	22,307	19,235
Ca	15,115	75,174	63,828	Ni	76	58	98
Cd	6	2	5	P	1,013	511	985
Co	2	5	5	Pb	14	7	13
Cr	67	16	67	S	127	27	1,593
Cu	11	106	100	Si	48,646	439,644	45,3749
Fe	23,327	103,048	100,199	Sr	238	95	223
K	5,356	12,584	10,442	Ti	1,901	18,978	17,797
Zn	66	25	59	V	127	259	249

3. Results and discussion

3.1. Chemical speciation and functional groups

The use of VA for further applications prior requires the chemical characterization to understand the whole properties related to their composition. The concentration of all elements in the volcanic ash samples obtained from ICP-OES is presented in Table II. The pollutants like Ag, As, Mo, Sb, Se, and Ti and light elements like Be and Li were not detected. In samples P1, P2, and P3, the first and second dominant elements are Si and Fe, respectively, followed by Al and Ca. The soil nutrients like K and P are also found with a significant concentration in all samples. The transition metals such as Cd, Cu, Co, Ni, Pb, and Zn are present with low concentrations contrary to Mn and Mg, whose concentrations are significant. As well, the presence of S is also noticed. Elevated concentrations of Cr, Ni, and V found in some rocks samples from Mount Cameroon can be due to the basaltic composition of parent rocks since basalts are enriched in Fe-family elements (Ti, V, Co, Ni, Cr) [2, 19] . During the soil formation, the loss of some major elements favors these Fe-family elements, and they can also be affected by the soil age [20].

In general, the values of the above elements obtained in this study are higher than those in [21] from the normal landfill soils in Buea (Cameroon). It was proven that Cd, Cu, Ni, Pb, and Zn can adversely affect the growth of root grass in concentrations in the range of 40 to 50 mg Kg^{-1}, while on the contrary, lower concentrations in the range of 5 to 20 mg Kg^{-1} can stimulate the growth of the shoots [22]. Since our VA samples are product of the eruption of CVL of Mount Cameroon volcano, the high concentration values of these metals can be understood because of their origin. Manga *et al.* [2] found a similarly elevated amount of these metals for the VA along the lower slopes of CVL. The low values of Pb may be attributed to their removal through the crops by plant uptake mechanism. On the contrary, elevated Cu and Cd values can be assigned to agricultural activities and waste decomposition accumulation.

The value of Mn and Mg were found up to 2,772 mg Kg^{-1} and 3,637 mg Kg^{-1} in Guangxi and Morroco mining zones, respectively [23, 24], which are considerably higher than ours. It is worth noting that our samples are the VA products coming from a volcano eruption and cannot be directly compared to the uncontaminated soils. However, the tentative comparison leads to the conclusion that some of our sampling soils can be contaminated by some elements like Cd, Cu, and Cr and deficient for B, P, and Zn. The contamination can be justified by the elevated amount of the products ejected during the eruption of the volcano and to the industry activities developed in the area. The deficiency can be due to the constant removal of these elements by the plant growth process since these soils are used for agricultural activities. On the one hand, the dominant values of Si, Fe, and Al lead

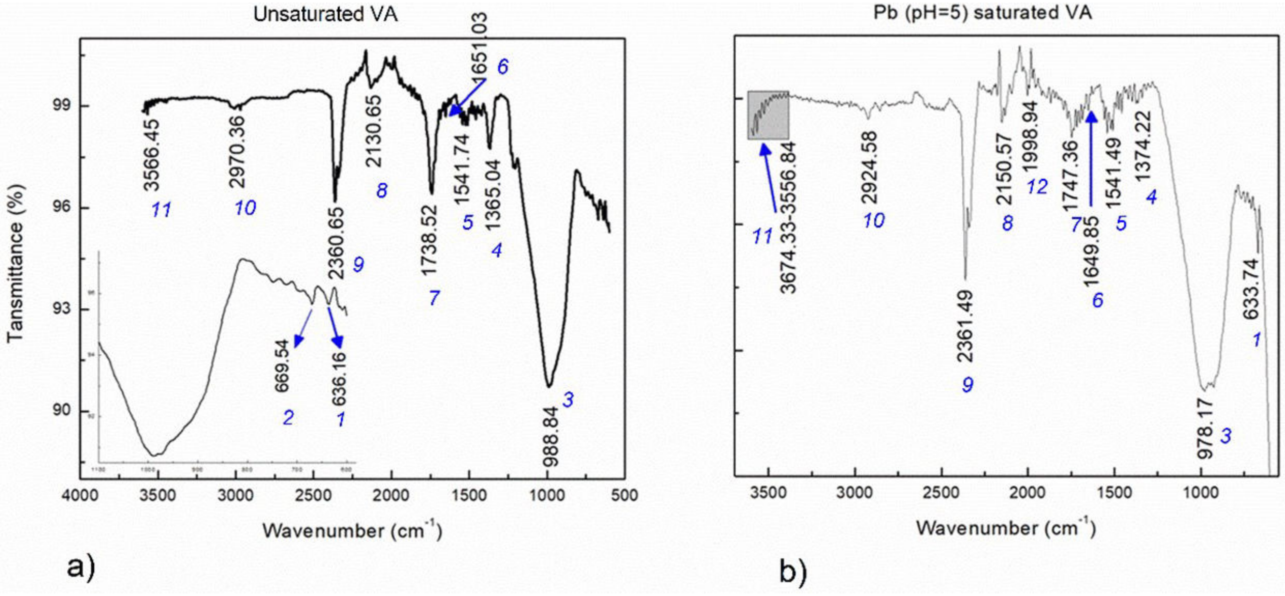

FIGURE 2. Normalized Fourier Transform InfraRed spectrum of unsaturated VA with the assigned peaks and their corresponding energies in eV, for unsaturated a) and Pb-saturated VA b). The insert is shown to highlight the weak peaks in the high region.

to their use in the construction area for manufacturing cement, Al, and Fe products. The samples can be used as adsorbents to remove pollutants such as Pb, Cr, etc.

According to the US EPA international method [16], the leaching tests performed with deionized water and measured by ICP-OES showed that our VA samples have the potentiality to adsorb Al, B, Li, and S. It was observed a non-significant release of Ca, K, Mg, Na, Ni and Pb into the water with a difference of about 0.01 to almost 0.5 from Ca and 0.1 mg L^{-1} for Pb compared with deionized water. The elements As, Cu, P, Mg, V, and Zn are not released. The release of such elements can facilitate the retention of metals present in aqueous solutions by ion exchange process. Similar results were found by Botto *et al.* [5] for VA from Puyehue Cordon Caulle Volcanic Complex (Chile) collected at Villa La Angostura using for the removal of As. These results could be a good signal for the removal process using our studied VA in the natural form.

Infrared spectra of VA samples saturated and unsaturated with Pb^{2+} (Fig. 2) showed mainly peaks corresponding to the deformation of M-OH functional groups (M = Mg, Al, Fe) or Si-O stretching vibrations [4, 25]. Also, those corresponding to the Si-O/Al-O from aluminosilicate framework and/or P-O stretching vibrations from polyphosphates [4,25], C-O stretching and bending vibrations from carbonate groups [26]. In general, minimal differences in the transmittance intensity of these peaks were observed, indicating changes in VA during the Pb^{2+} adsorption process; however, characterization of the saturated and unsaturated materials by other techniques is necessary to establish the mechanism by which Pb^{2+} is adsorbed on these materials.

3.2. Adsorption capacity of VA to remove lead in aqueous solution

The adsorption capacity of VA for the removal of Pb^{2+} at the solution pH 3, 4, and 5 are shown in Fig. 3 for the three samples P1, P2, and P3. The maximum adsorption capacity (7.59 mg g^{-1}) is obtained from P1 at pH 5, whereas the minimum (1.49 mg g^{-1} at pH 4) is from P2. It is observed that in P1, the adsorption capacity increases with the increase of pH, while in P2 and P3, a slight decrease is observed from pH 3 to 4. However, the increase is noticed at pH 5.

The comparison was elsewhere made based on the selection scale of low (*e.g.*, 10 mg L^{-1}) and high (*e.g.*, 200 mg L^{-1}) residual concentration. For that purpose, the adsorption capacity of VA for Pb^{2+} from P2 and P3 at all pH are in good agreement with results ($\sim$1.5-4.75 mg g^{-1}) of Ref. [10]

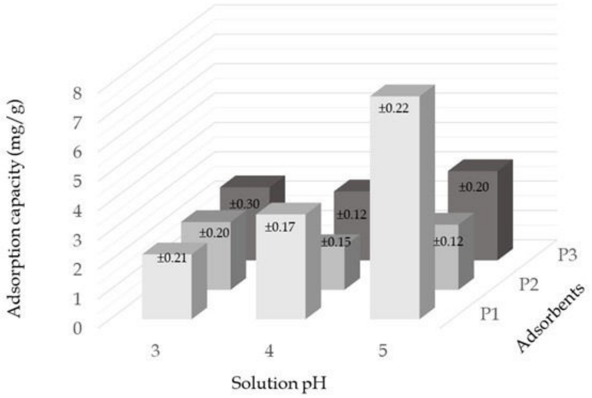

FIGURE 3. Trend of VA adsorption capacity (mg g^{-1}) for the removal of Pb^{2+} in aqueous solution. The experiments were performed in triplicate, and the average value of the adsorption capacity and the standard deviation value is shown.

obtained at pH 4.9 with smectite material as an adsorbent in the Pb (II) concentration range of 50-130 mg l^{-1}. As well, the comparison can also be made with some biomass of marine algae like cadium taylori from Australia (9 mg g^{-1}) and padina gymnospora from Rio de Janeiro (4.3 mg g^{-1}) given in Ref. [27]. More to that, the maximum adsorption capacity can be compared with that (6.8 mg g^{-1}) obtained on kaolinite material at pH 5 but at the concentration of 2,000 mg L^{-1} [28]. On the other hand, our results are low compared to those reported on Jordanian Kaolinite and Tunisian Smectite, respectively, by Al-Harahsheh *et al*. [29] and Eloussaief *et al*. [30]. They respectively reported the adsorption capacity of 13.32 mg g^{-1} at pH 5 with the concentration of 131.32 mg L^{-1} and 75.35 mg g^{-1} at pH 5.5-6.5 with 25-275 mg L^{-1} of concentration range. On the contrary, the results of Dawodu *et al.* [31] obtained on Agbani clay in the concentration range of 20-100 mg L^{-1} at pH 6 are too low ($\sim$0.2-0.82 mg g^{-1}) compared to ours.

The knowledge of the surface charge is necessary for the understanding of the adsorption process onto the VA material. For these reasons, the zero point of charge pHZPC was determined by titration method according to [32]. The pHZPC of P1, P2, and P3 was 7.64, 7.57, and 7.25, respectively, almost neutral. It is known that the surface of the adsorbent sample is positively charged below pHZPC, suggesting that the adsorbent surface favors the electrostatic attraction with anions [12, 32]. The surface is neutral at pHZPC. The results show that Pb^{2+} cations were better removed at pH $5 <$ pHZPC, with an adsorption capacity of 7.60 mg g^{-1}. Knowing that the electrostatic attraction with anions is predominant in that range, one can attribute the adsorption process to the ion exchange mechanism in which Pb^{2+} was exchanged with another cation (maybe Ca^{2+} or Mg^{2+}, etc.) on the surface. Leaching tests showed that these elements are little released and can contribute to the adsorption process. The surface of P1 has a higher pHZPC than that of P2 following P3. These preliminary adsorption results certify that our VA soils in the natural form can be used as adsorbents for pollutants removal.

The value of 1,028.11 mg Kg^{-1} was obtained from ICP-OES analysis for Pb concentration onto unsaturated P1. Since sample P1 has a high adsorption capacity, it was chosen for further experiments (XANES). This concentration is considerably increased in Pb-saturated samples. This result also suggests a slight change in the chemical composition for the adsorbed samples.

3.3. XANES results

Figure 4a) presents the normalized XANES absorption spectrum at Pb L3 edge of Pb-SVA-P1 compared to the spectra of some selected reference compounds ordered by their E$_0$ energy shift determined as the maximum of the first derivative. The experimental energy edge of Pb-SVA-P1 is at 13,035.82 eV which is a little higher value than the theoretical Pb L3

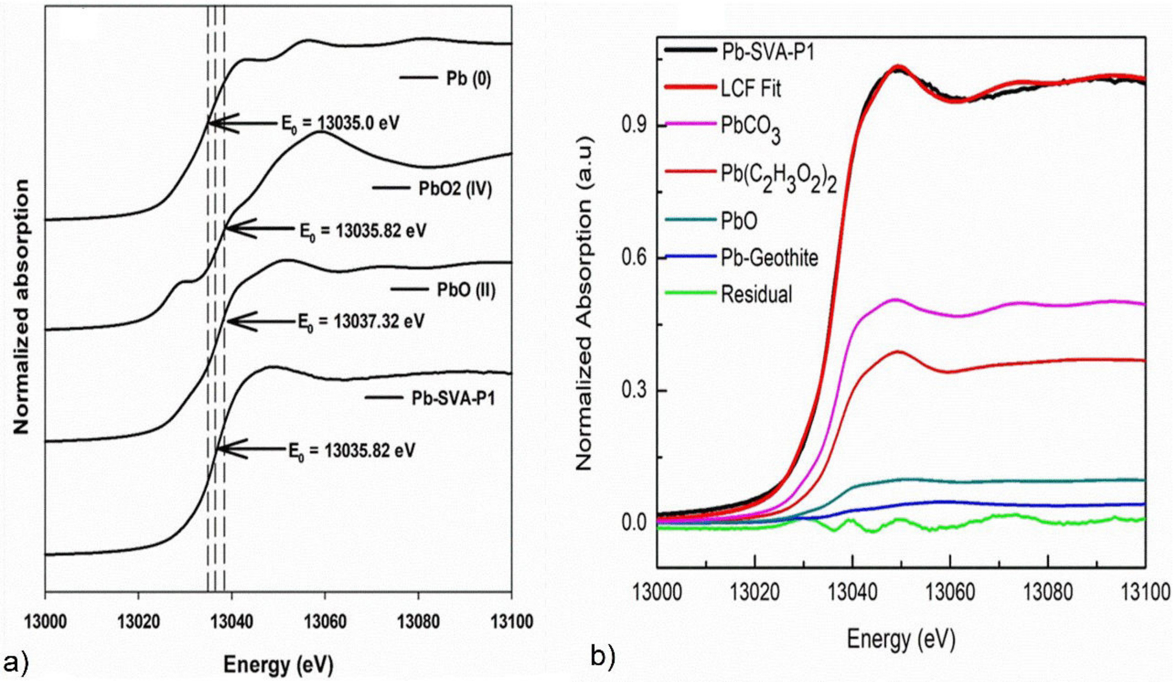

FIGURE 4. a) Pb XANES spectra of Pb-SVA-P1 and reference compounds: Lead metal (Pb; (0)), Lead monoxide (PbO; (II)), and lead dioxide (PbO2; (IV)). Dotted lines show the E$_0$ of model compounds. The number in parenthesis indicates the oxidation states. b) Linear combination analysis of Pb L3 XANES spectra of sample Pb-SVA-P1 using reference compounds: lead monoxide (PbO), Pb acetate (Pb(C$_2$H$_3$O$_2$)$_2$), Pb carbonate or cerussite (PbCO3), and Pb-goethite (Pb-α-FeOOH). The residual expresses the difference between the experimental and theoretical curves obtained after fitting. R-factor is 0.0009 and $\triangle$E$_0$ is -0.509 eV.

edge energy (13,035 eV). Pb saturated VA reaches its edge energy after metal, at the same level of PbO and just before PbO_2 suggesting an oxidation state of +2. According to these observations, it is concluded that the oxidation state of lead used for adsorption experiments (that was +2) is kept constant, and the Pb-SVA-P1 may content lead species in oxidation state (II).

The normalized spectrum of Pb-SVA-P1 is similar to that of PbO, suggesting that Pb(II) in the volcanic ash has the same geometry as PbO in which Pb(II) is in a pyramidal coordination. The XANES study of cement also showed that Pb(II) in the cement samples is mainly in a pyramidal coordination [33]. This can be compared with the volcanic ash materials, which have been proven to be efficient in cement production in the construction sector [3, 4]. It is known that XAS at the Pb-L3 edge is assimilated to an electronic transition from the 2p core electron to an unoccupied orbital. Because of the dipole selection rule, normally, all electronic transitions are not allowed between the 2p level to unoccupied orbitals. Nevertheless, the characteristic of the main peak in the derivative spectrum of Pb-SVA-P1 suggests possible electronic transitions between 2p $\rightarrow$ 6d and/or 2p $\rightarrow$ 6s unoccupied orbitals. However, in C4v symmetry in a pyramidal geometry, the hybridization between the Pb(II) 6s and 6p orbitals can create vacancies in the 5_{a1} level allowing the 2p $\rightarrow$ 6s transition as described in Refs. [33, 34] . Since the quadrupole 2p-6d transition occurs with a low probability while the dipolar 2p-6s occurs with a high probability, one can propose that in the investigated VA materials, the electronic transitions occurring could be assimilated to 2p $\rightarrow$ 6s.

A PCA was applied to determine the suitable standards likely to be present in VA and useful to perform LCF analysis. The lead compounds PbS, PbO, PbO_2, Pb_2O_4, $Pb(CO_3)$, $Pb(SO_4)$, $Pb(C_2H_3O_2)_2$, and Pb-Goethite (Pb-α-FeOOH) were used as standards for that purpose. The choice of these standards was guided by the literature reviews concerning the composition of VA [4, 35, 36]. The PCA analysis was first performed to check the standards likely to be present in the sample. According to the literature, those that are not likely to be present in the VA samples and the PCA check results were discarded. The next step was performed using all standards potentially likely to be present. The results suggested that the main components of VA are Pb carbonate, Pb acetate, and Pb oxide II in addition to Pb- goethite.

An LCF shown in Fig. 4b) was performed on sample Pb-SVA-P1 using a set of four reference compounds proposed by PCA, representing: Lead associated to organic matter ($Pb(C_2H_3O_2)_2$), lead associated to carbonate or cerussite ($PbCO_3$), lead monoxide (PbO) and lead associated to iron oxyhydroxides (Pb-goethite, Pb-α-FeOOH). The use of goethite was to check a possible interaction between hydroxyl and lead. The residual curve is as good minimized, suggesting that the analysis of the Pb XANES signature may be explained principally by the contribution of Pb associated with: carbonate (44.4%) $>$ organic matter (34.5%) $>$ monoxide (14.7%) $>$ iron oxyhydroxides (6.4%). This suggests that a certain amount of minor Pb species may be present in the studied samples at a negligible percentage.

The major components are cerussite and Pb-organic matter due to the C-O or O-H functional groups related to CO_2 and/or to water molecules formed during VA weathering and adsorption. Additionally, Somasundaram *et al.* [35] also revealed the high concentration of carbonate and organic matter bound-Pb in soil samples, and Denys *et al.* [36] showed that the occurrence of cerussite in soils strongly control the Pb-bioaccessibility.

These results show that there is an interaction of the sorbed element (Pb) with some groups (probably related to hydroxyl or water molecules) of the surface of the VA samples. The presence of cerussite, Pb acetate, and Pb monoxide can be explained by both micro precipitation and adsorption over the groups of the materials. Since the LCF showed a significant contribution of cerussite, lead acetate, and lead monoxide, we can propose microprecipitation and ion exchange as the main mechanism. As the VA surface is repelling cation, the possibility for another Pb to be coordinated or interact with the sorbed Pb is to replace one of the exchangeable cations (like Ca^{2+}, K^+, Na^+, Mg^{2+}), or probably a part of the aggregates of PbO over the particles. In addition, leaching tests performed by ICP-OES have shown that about 12.65% of alkali elements (Na^+, K^+) and 90% of alkaline (Ca^{2+}, Mg^{2+}) were released in VA. This might suggest a possibility of ion exchange as one of the adsorption mechanisms for Pb sorbed onto VA [37].

4. Conclusions

The present study shows that the VA from the CVL of Mount Cameroon volcano can also be used as an economically sustainable adsorbent for removing pollutants from contaminated water. Furthermore, XANES results confirm that the Pb-adsorbed from the solution in the presence of VA is in the oxidation state +2 and that Pb-SVA-P1 is mainly composed of lead associated with carbonate, acetate, monoxide, and goethite. The results showed that the lead removal occurred mainly by microprecipitation of lead acetate and carbonate (cerussite) and a possible ion-exchange forming lead monoxide. It is herein proven that XANES can depict the adsorption mechanism and determine the chemical components present in an unknown sample. It thus might appear as a powerful characterization tool for adsorbent materials containing heavy elements.

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Conflicts of Interest

The authors declare that there is no conflict of interest.

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