The use of volcanic ash for the sorption of metal elements: Characterization by x-ray absorption spectroscopy technique

Prof. Bridinette Thiodjio Sendja

National Advanced School of Engineering of Yaounde
University of Yaounde I, Yaounde-Cameroon

sbridine@yahoo.fr

School on Synchrotron Light Sources and their Applications
Virtual ICTP-Italy, 23 january to 03 february 2023

Plan

Introduction

I-Review basics of x-ray absorption spectroscopy (XAS) theory

II-Basic notions on volcanic ash materials

III-Location of Cameroon volcano and sampling area

IV-Adsorption experiments for metal (Fe, Pb, Cr, Se) sorption

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

- Adsorption capacity
- Oxidation state by XANES
- Chemical composition by XANES
- Structural properties by EXAFS

Conclusion

Introduction

Objective of XAS

an understanding of physical properties of materials based on knowledge of their local structure

- X-ray absorption spectroscopy (XAS) provides electronic, chemical and structural information on the material through the spectrum of x-ray absorption coefficient.
- Determination of: chemical environment and composition, number and type of its neighborhood atoms, interatomic distance, structural disorder.
- Does not require a long-range order (distance from 5 to 10 Å radius).
- Selective technique for a specific element.
- Appropriate to: amorphous and crystalline; solid, liquid and gas.

In this presentation, XAS is applied to characterize the metal sorbed volcanic ash (VA) materials **with the aim to understand their physical properties**.

- Those used in this work are from the Cameroon volcanic line collected at Djoungo in Littoral region in Cameroon.
- They are used to adsorb Fe, Pb, Cr and Se from aqueous solutions.
- Application in wastewater treatment.

I-X-ray absorption spectroscopy (XAS)

Interaction between matter and radiation

Fig.1

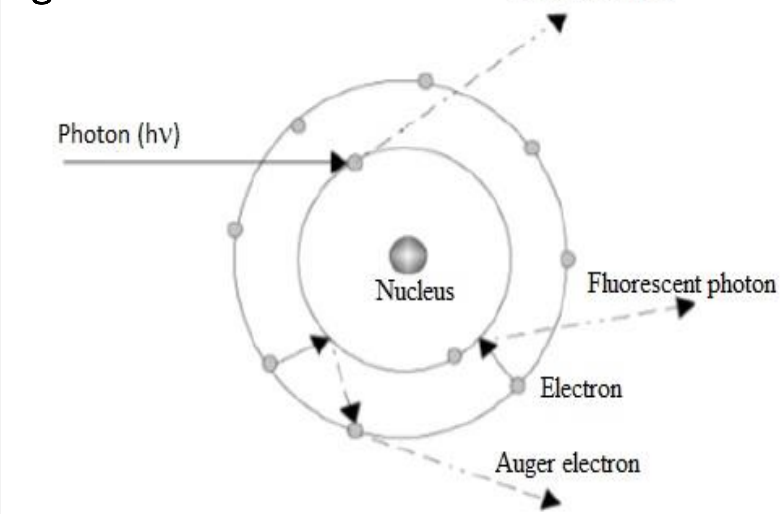
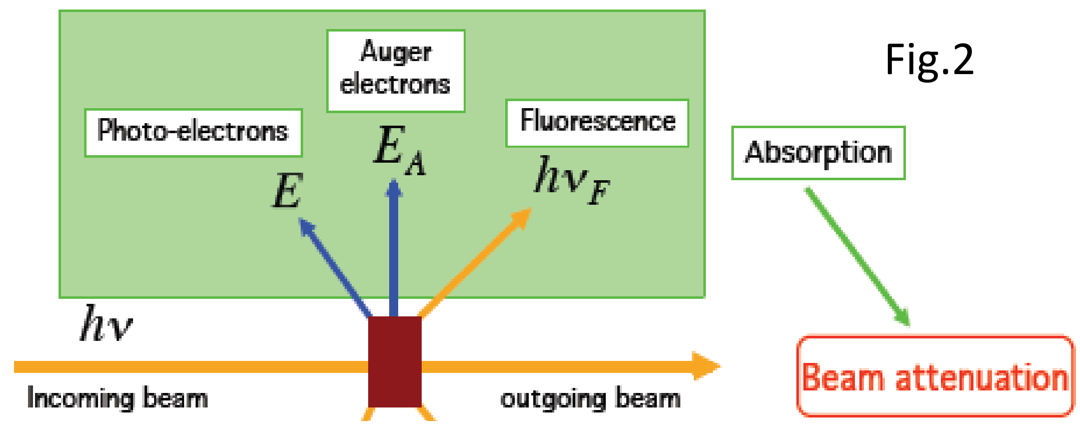


Fig.2



I-X-ray absorption spectroscopy (XAS)

Interaction between matter and radiation

Loose of energy through decay processes

Fig.2

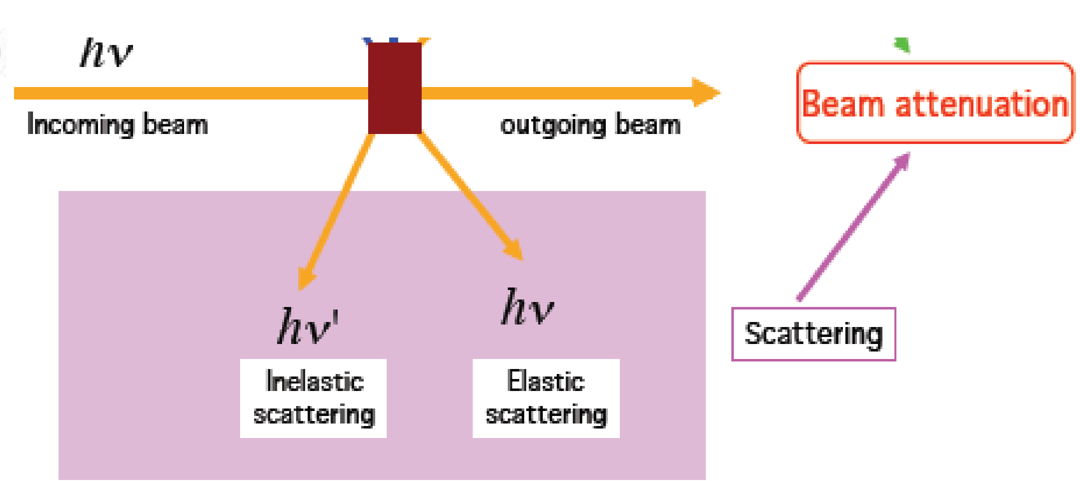
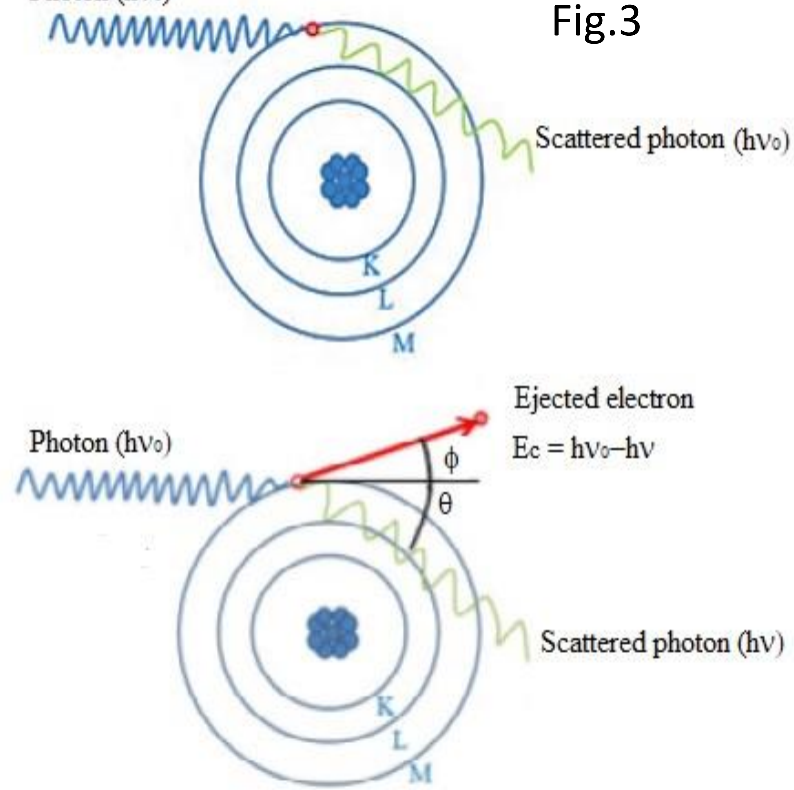


Fig.3



I-X-ray absorption spectroscopy (XAS)

Beam attenuation of x-ray

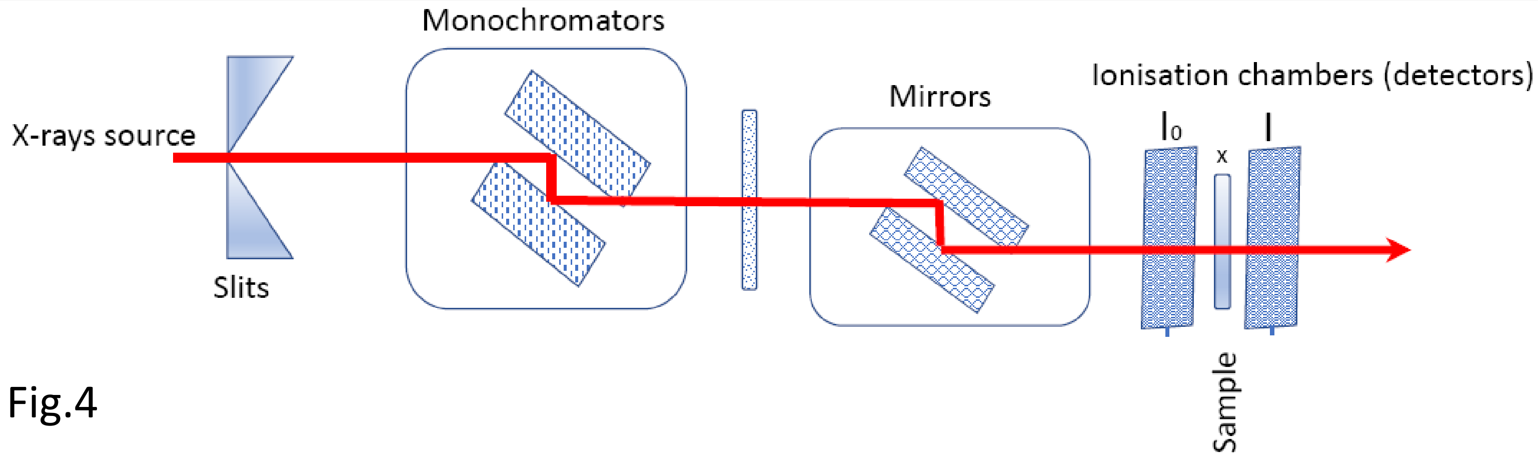


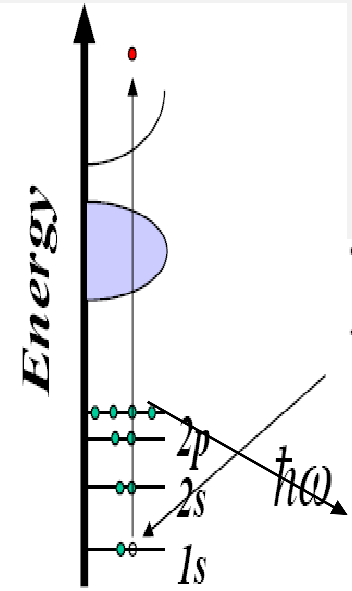
Fig.4

Exponential attenuation of x-ray: Beer-Lambert law → $I = I_0 \exp(-\mu x)$

Attenuation absorption coefficient → $\mu x = ln\frac{I_0}{I}$

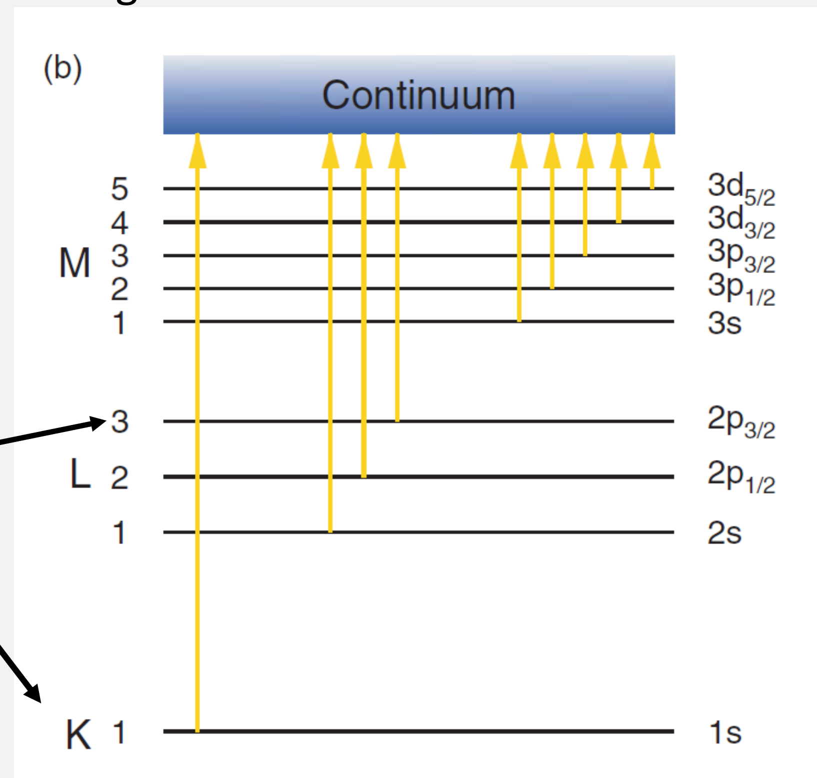
I-X-ray absorption spectroscopy (XAS)

Absorption edges



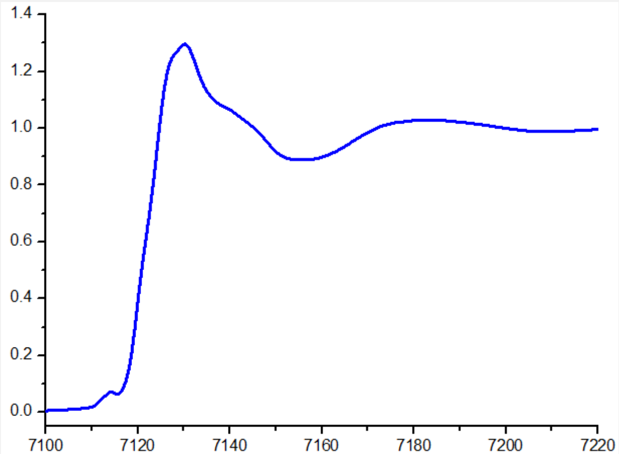
Edge	Configuration
K	1*s*
L_1	2*s*
L_2	$2p_{1/2}$
L_3	$2p_{3/2}$
M_1	3*s*
M_2	$3p_{1/2}$
M_3	$3p_{3/2}$
M_4	$3d_{3/2}$
M_5	$3d_{5/2}$

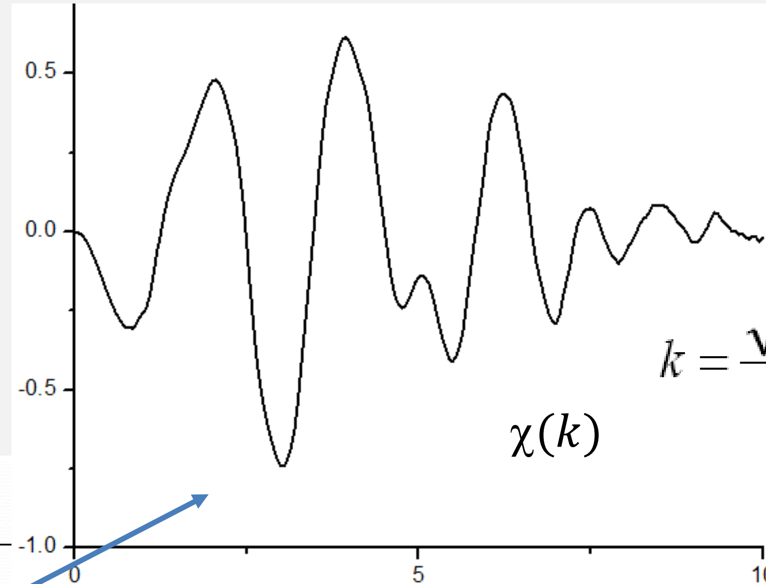
Fig.5



I-X-ray absorption spectroscopy (XAS)

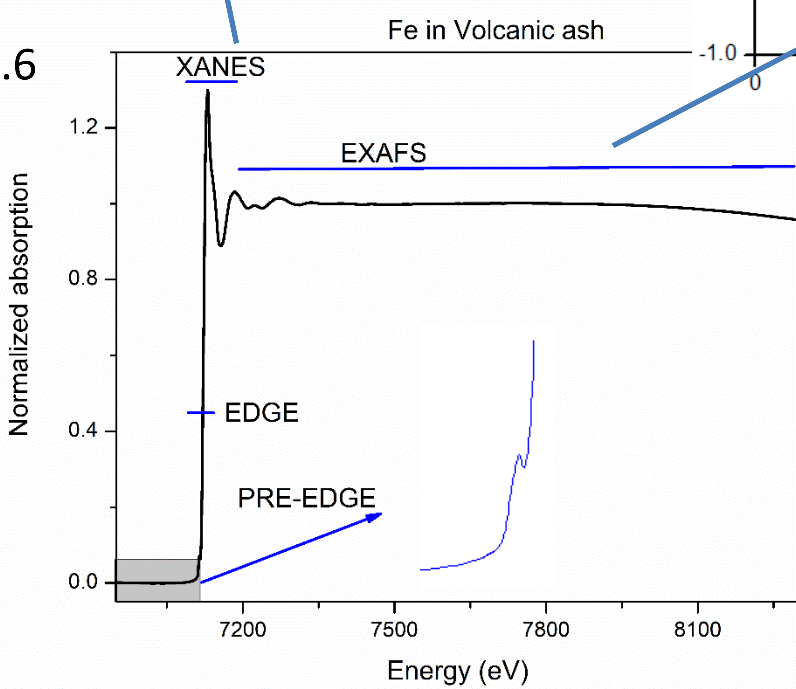
Regions of x-rays absorption spectrum





$$k = \frac{\sqrt{2m(\hbar\omega - E_B)}}{\hbar}$$

Fig.6



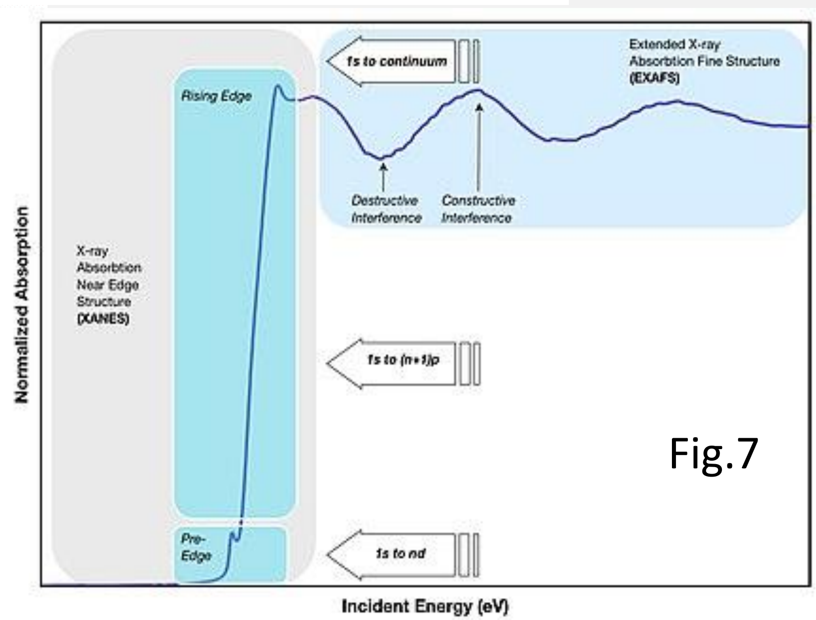


Fig.7

I-X-ray absorption spectroscopy (XAS)

EXAFS equation

From *ab-initio* calculations or from reference compounds

$$\chi(k) = S_0^2 \sum_{j=shells} N_j A_j(k) \, Sin[2kr_j + \overbrace{\varphi_j + 2\delta_1}] e^{-2k^2\sigma_j^2}$$

Measure → Coordination number

Interatomic distance

Debye Waller factor
-Thermal vibration
- Static disorder

Fig.8

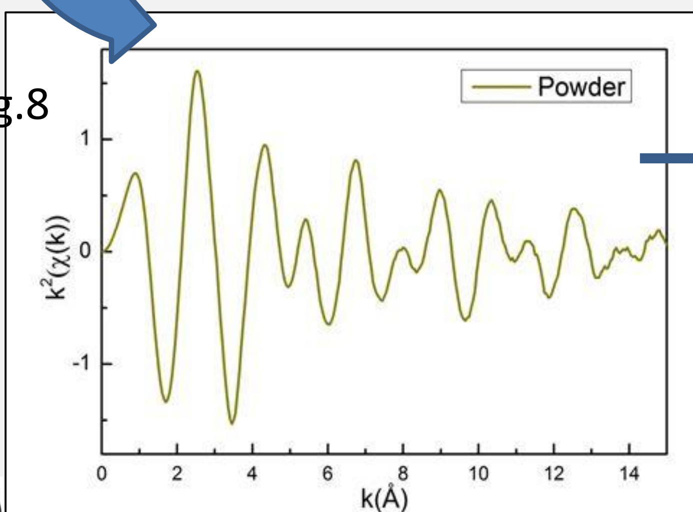
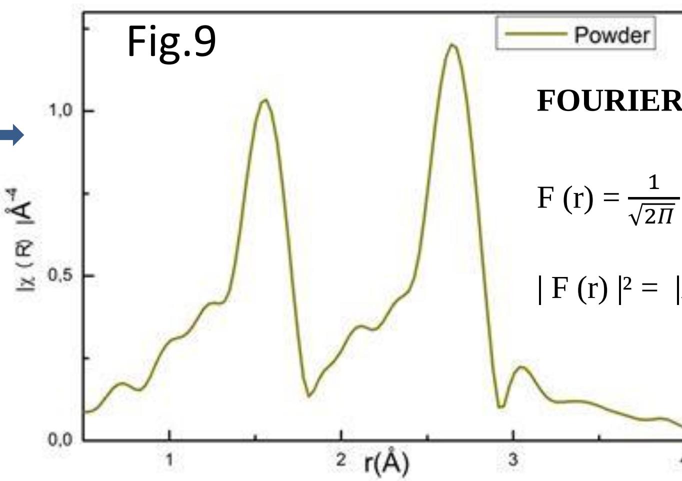


Fig.9



FOURIER Transform function

$$F(r) = \frac{1}{\sqrt{2\Pi}} \int_{k_{min}}^{k_{max}} \chi'(k) \, e^{2ikr} \, dr$$

$$|F(r)|^2 = |R_e(F(r))|^2 + |I_m(F(r))|^2 = |\chi(r)|$$

I-X-ray absorption spectroscopy (XAS)

EXAFS equation

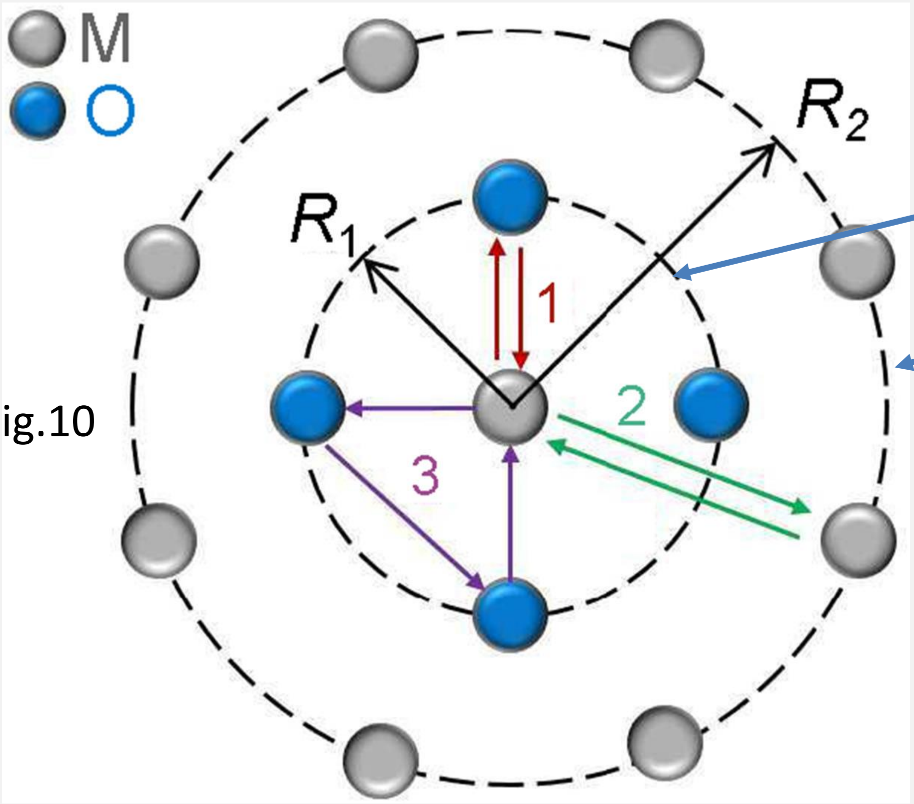
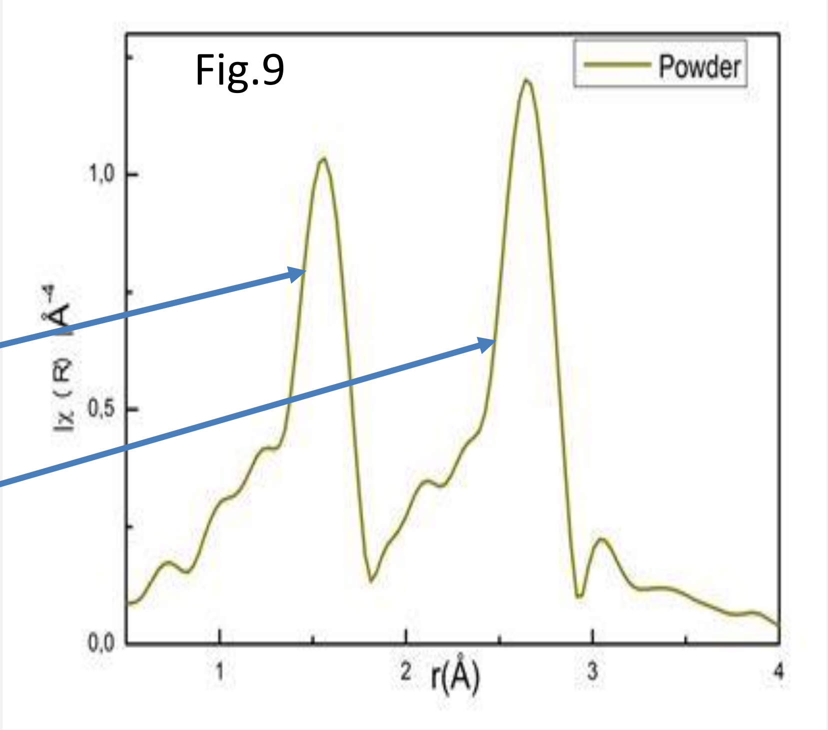


Fig.10

Fig.9



- ❑ A central absorbing atom surrounded by two coordination shells of four atoms at distance R_1 and eight atoms at distance R_2.
- ❑ Two direct scattering paths 1 and 2, multiple scattering paths such as 3 are possible.

II-Basic notions on volcanic ash materials

- Volcanic ash (VA) is a mixture of rock, mineral, and glass particles expelled from a volcano during a volcanic eruption.
- VA is part of the dark ash column that rises above a volcano during the eruption.
- The particles that make up VA can travel long distances, carried by winds.

VA can be dangerous.

- It can cause eye, asthma, nose, lung irritation, and cardiopulmonary problems to human and animals.

Despite its dangerous character, VA is also useful.

- The soils cover by the VA are fertile leading to the production of abundant food.
- It can also be used for skincare: for paste soap, hand soaps, and rubber erasers.
- It is used for producing cement for construction.
- It can be used as water filter resulting to a natural occurring filtration process during the rain.
- Thus, It can be used as adsorbent for the removal of some toxic element from aqueous solutions.

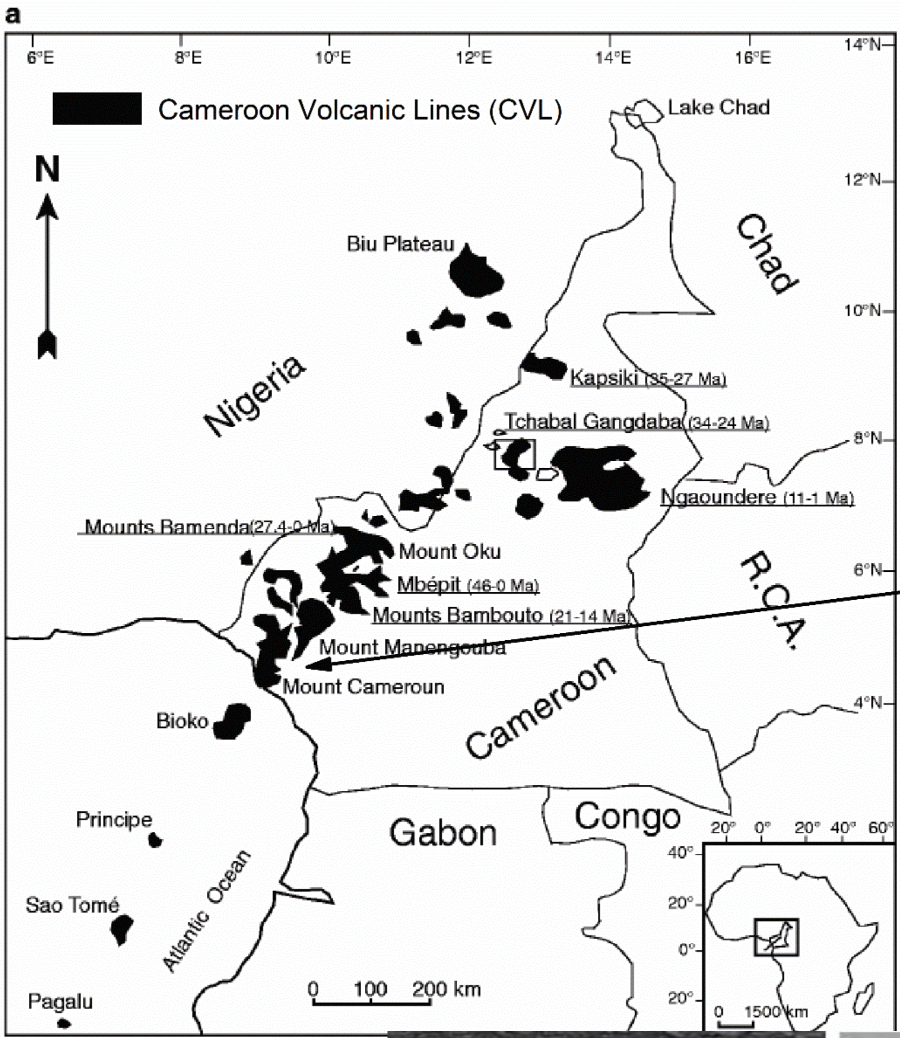
In our project, we used VA of Mount Cameroon for the removal of Fe, Pb, Cr and Se with the aim to investigate their physical properties in order to be used for wastewater treatment.

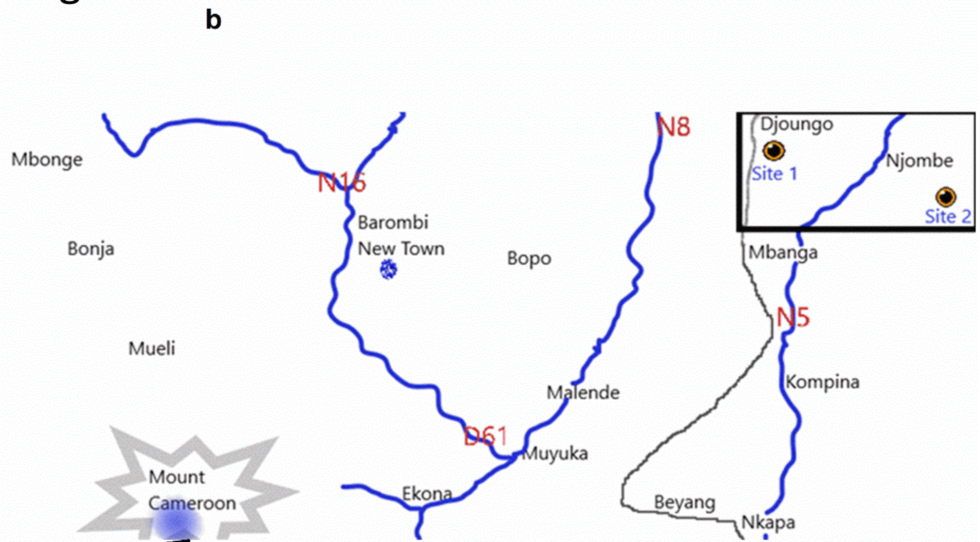
II-Basic notions on volcanic ash materials

- **Mount Cameroon** is an active volcano in the South-West region of Cameroon next to the city of Buea near the Gulf of Guinea.
- It is the highest point in sub-Saharan western and central Africa.
- The fourth-most Prominent peak in Africa, and the 31st-most prominent in the world.
- The most recent eruption occurred on February 3, 2012.
- Mount Cameroon is one of Africa's largest volcanoes, rising to 4,040 metres (13,255 ft) above the coast of west Cameroon.
- It rises from the coast through tropical rainforest to a bare summit, which is cold and windy.

III-Location of Cameroon volcano and sampling area

Fig.11



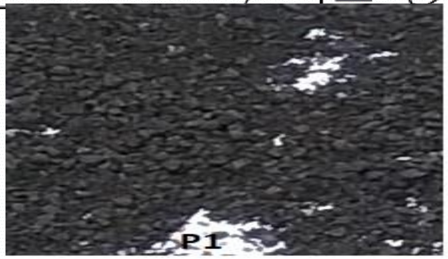


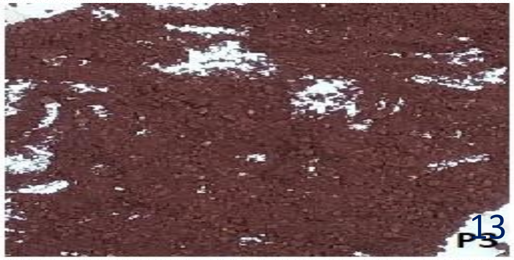
Eruption 2012

N. 04°35’12’’
E. 09°37’37’’
A. 140 ± 3 m

N. 04°35’33’’
E. 09°37’32’’
A. 147 ± 3 m

N. 04°35’09’’
E. 09°37’37’’
A. 134 ± 3 m





IV-Adsorption experiments for metal (Fe, Pb, Cr, Se) sorption

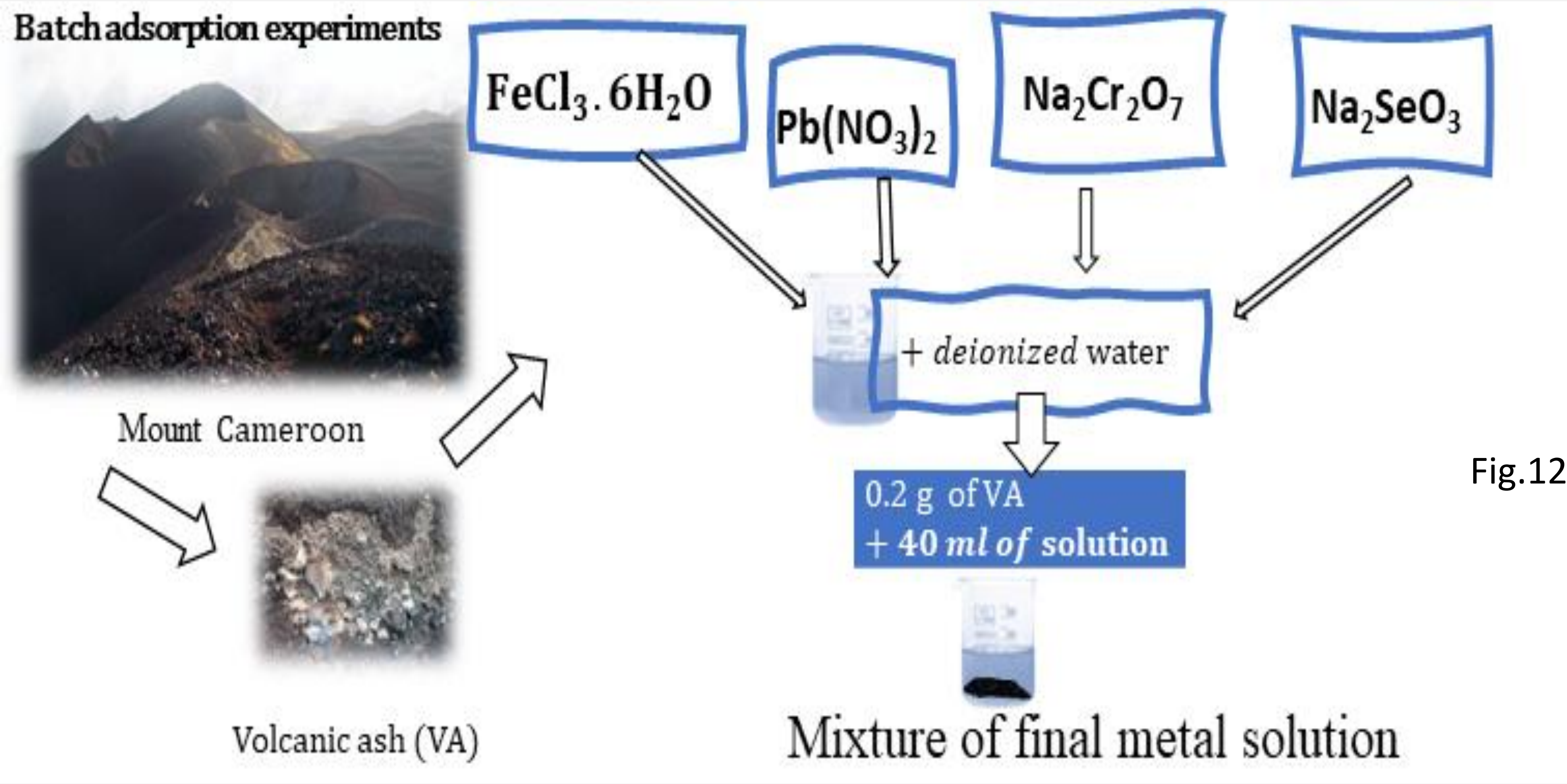


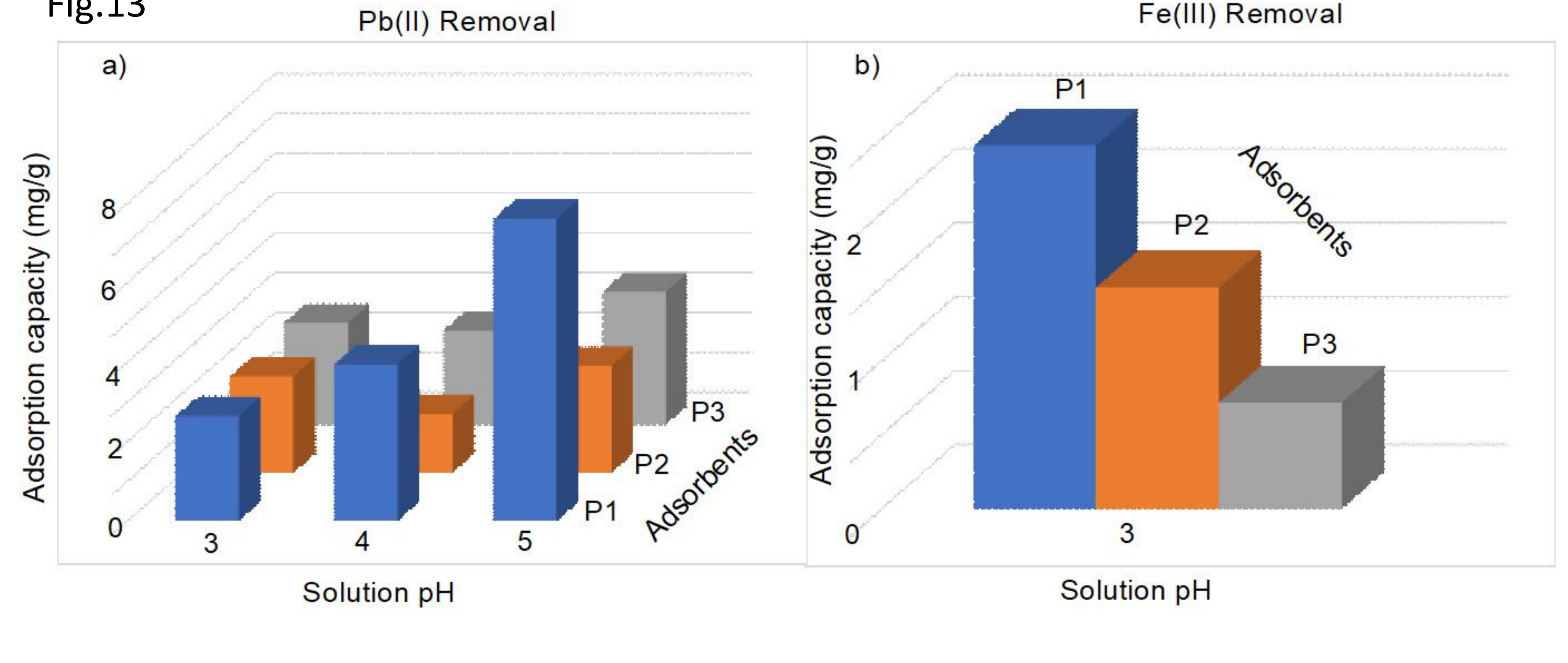
Fig.12

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Adsorption capacity

$$q = \frac{V\left(C_i - C_f\right)}{m}$$

Fig.13

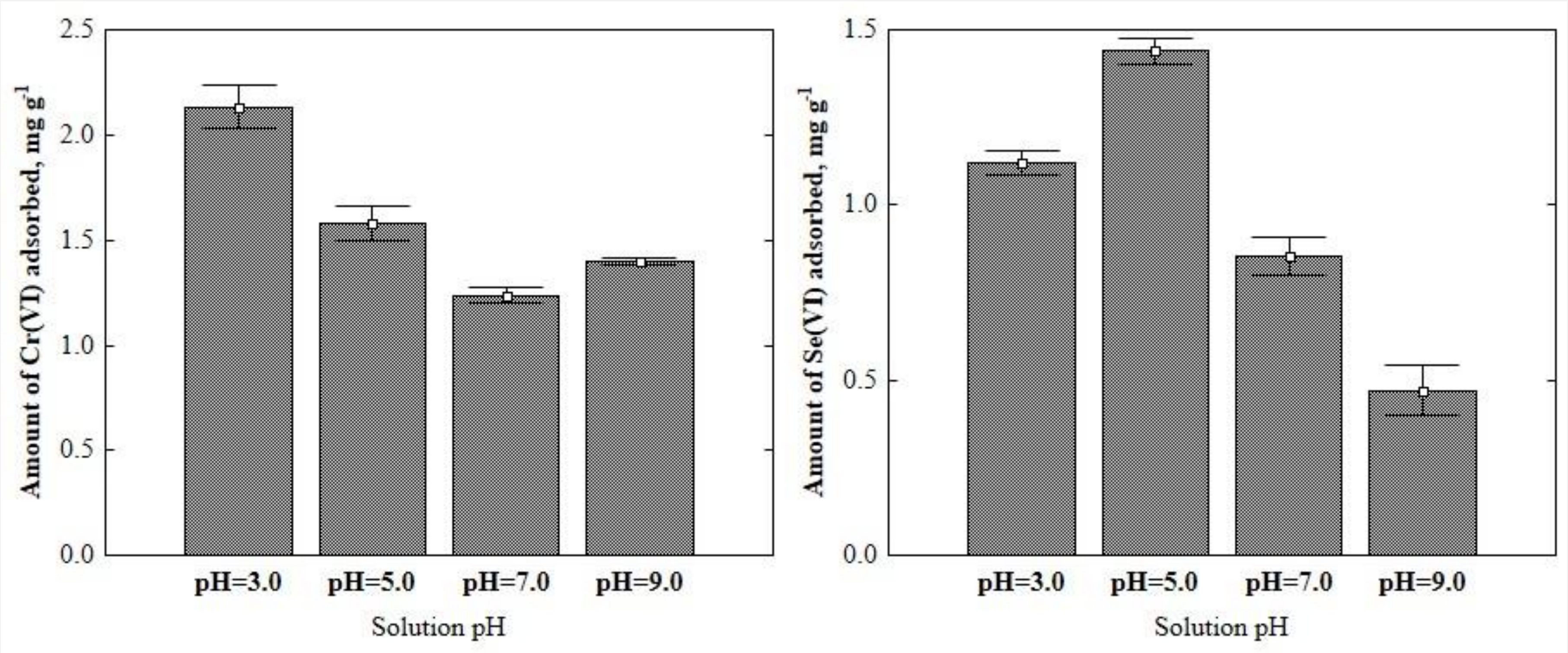


Zero-point charge pH (pH_{ZPC}) :
7.64, 7.57 and 7.25 for P1, P2 and P3

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Adsorption capacity

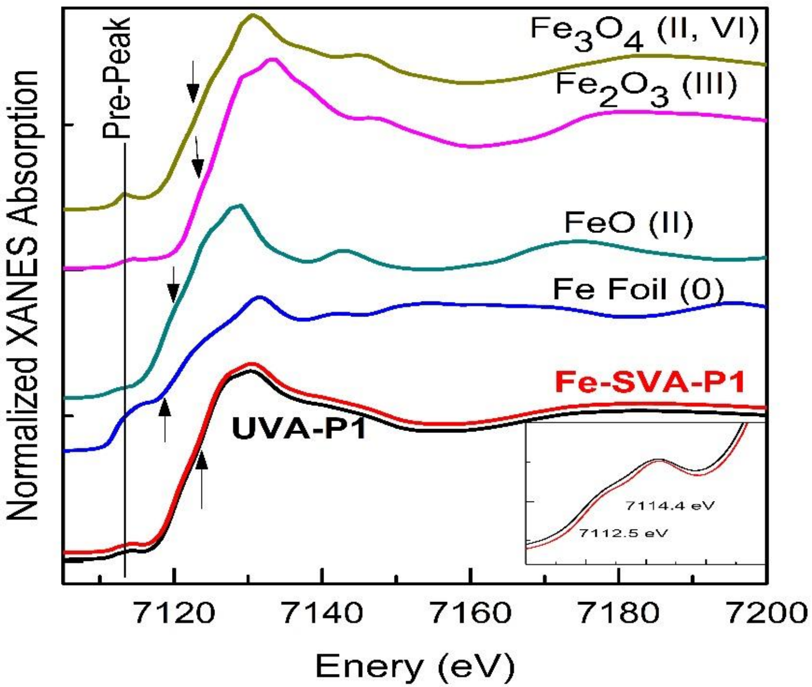
Fig.14

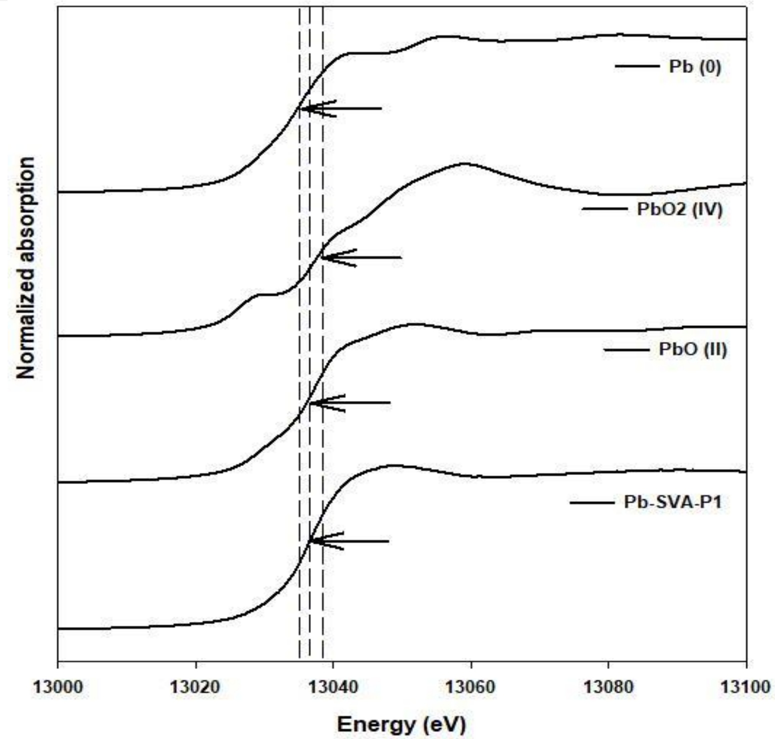


V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Oxidation state of VA by XANES

Fig.15





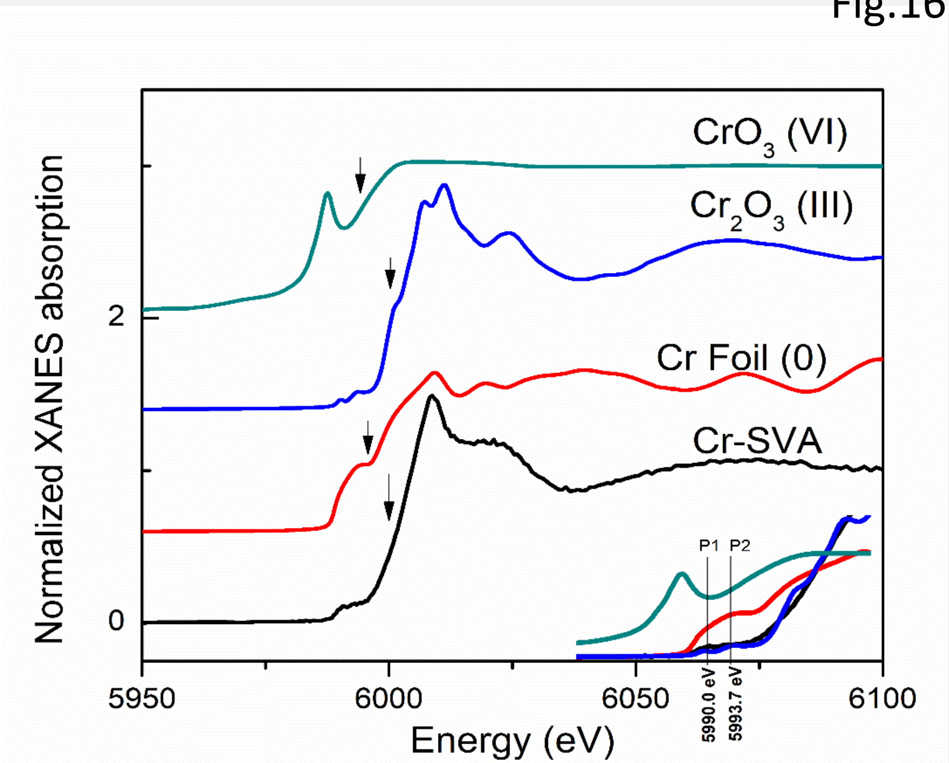
For iron sorbed VA
Oxidation state of VA is +3
No change

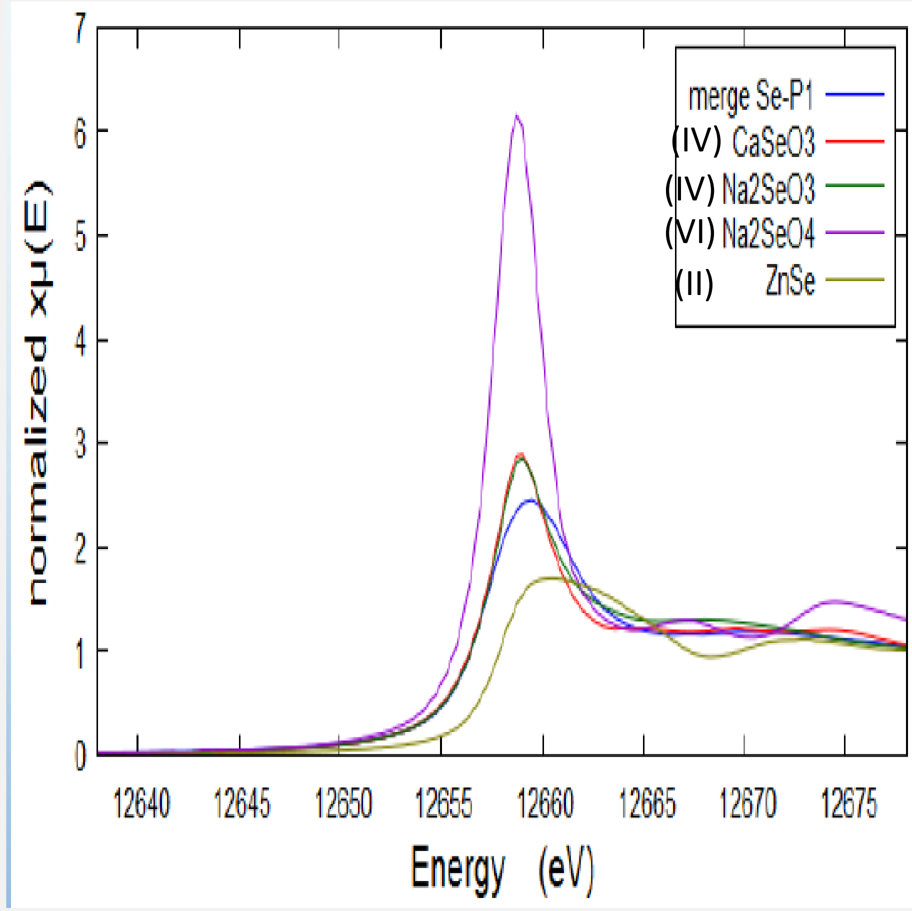
For lead sorbed VA
Oxidation state of VA is +2
No change

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Oxidation state of VA by XANES

Fig.16





For chromium sorbed VA

Oxidation state of VA is +3

Changes from +6 to +3

For selenium sorbed VA

Oxidation state of VA is +4

No change

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Linear combination fitting by XANES

- Chemical speciation in the VA metal edge XANES spectra was done by performing the LCF in an energy range of 20 eV to +30 eV around E_0.
- The Athena software was used.
- The reference compounds were used.
- To perform the LCF, a combination of at least four spectra of the selected standards was used to reconstruct the experimental VA spectra.
- The contribution of each standard is given in terms of percentages.
- The goodness of the fit is evaluated through the R_{factor}

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Chemical composition by XANES (LCF)

For lead sorbed VA

Main components: $R_{factor}=0.0009$

-lead monoxide (PbO)-wt 14.7(5%),

-lead acetate ($Pb(C_2H_3O_2)_2$)-wt 34.5(5%),

- lead carbonate ($PbCO_3$)-wt 44.4(6%)

-lead –iron hydroxide (Pb-α-$FeOOH$)-wt 6.3(0.3%)

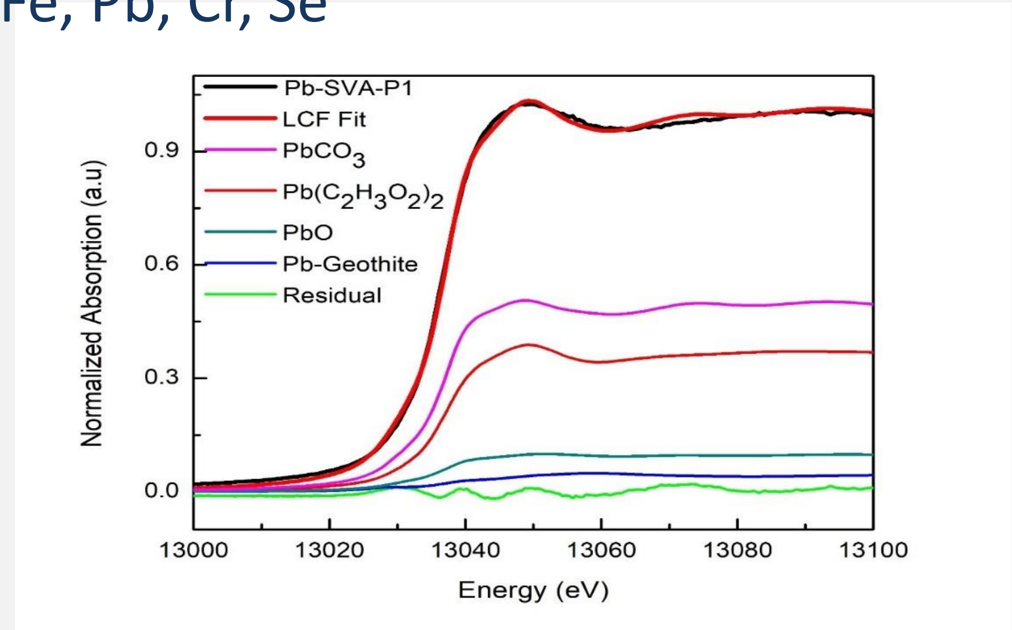
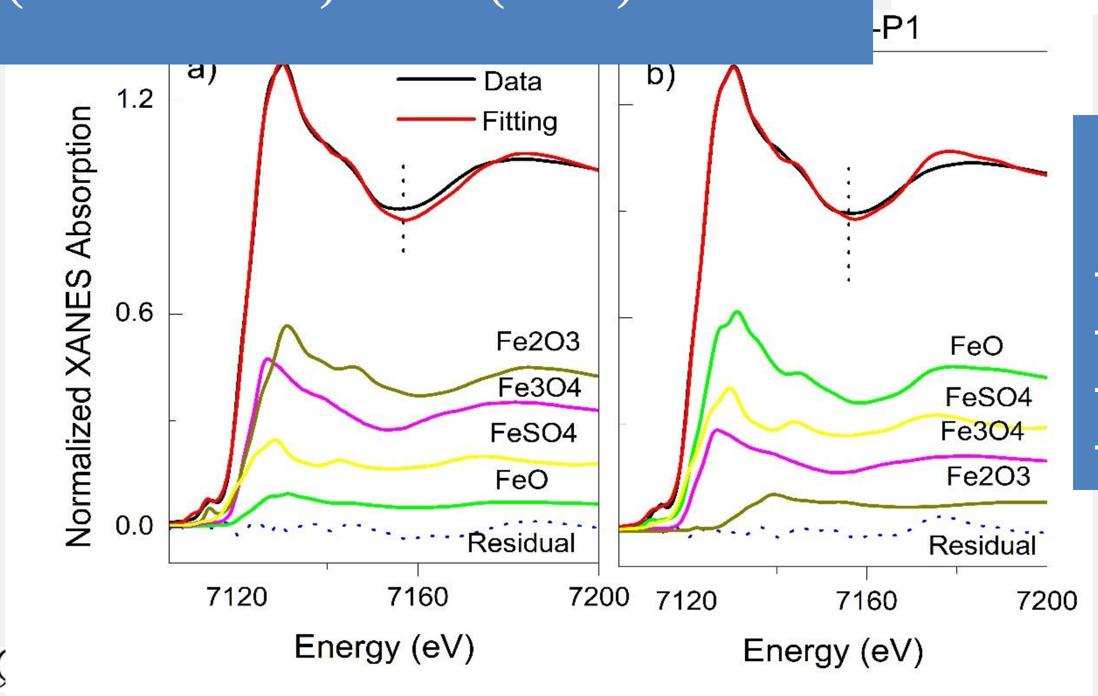


Fig.17



For iron sorbed VA

Main components: $R_{factor}=0.0028$

-iron sulphate ($FeSO_4$)-wt 27.1(0.9%);

-iron oxide (FeO)-wt 7.4(1.8%);

-Hematite (Fe_2O_3)-wt 21.3(1.4%)

-magnetite (Fe_3O_4)-wt 38.1(1.5%)

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Chemical composition by XANES

For chromium sorbed VA

Main components: $R_{factor}=0.002$

- Chromium(III) oxide (Cr2O3)-wt 47.9(3%),
- Iron(II) chromite (FeCr2O4)-wt 45.2(3%),
- Sodium dichromate (Na2Cr2O7)-wt 6.9(5%)

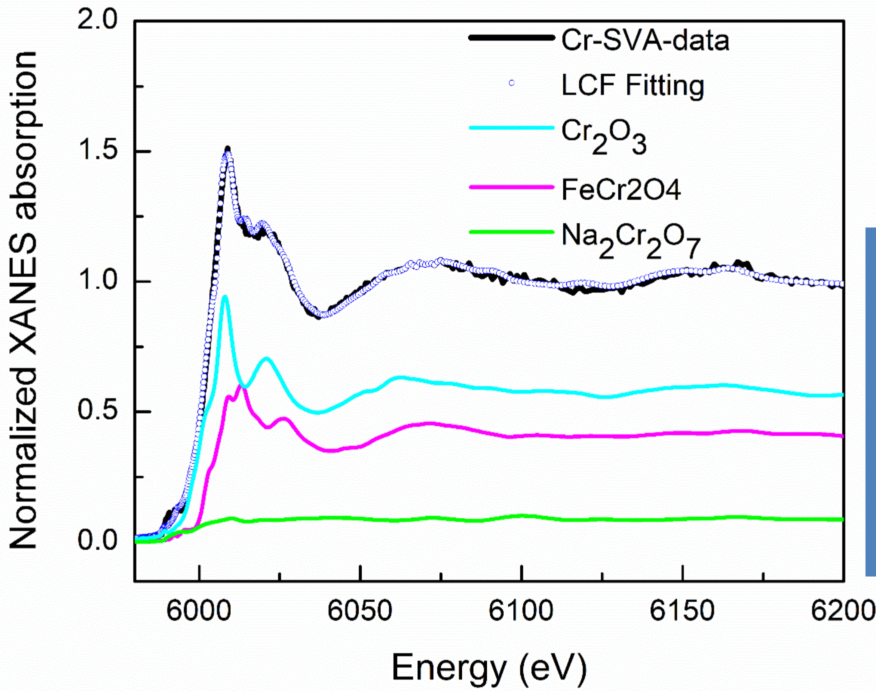
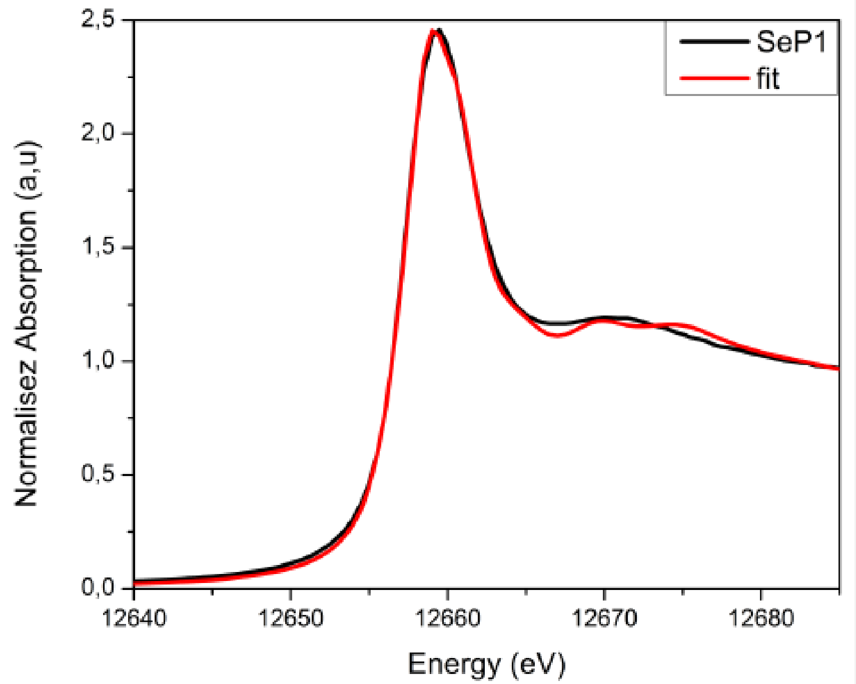


Fig.18



For selenium sorbed VA

Main components: R_{factor} 0.002

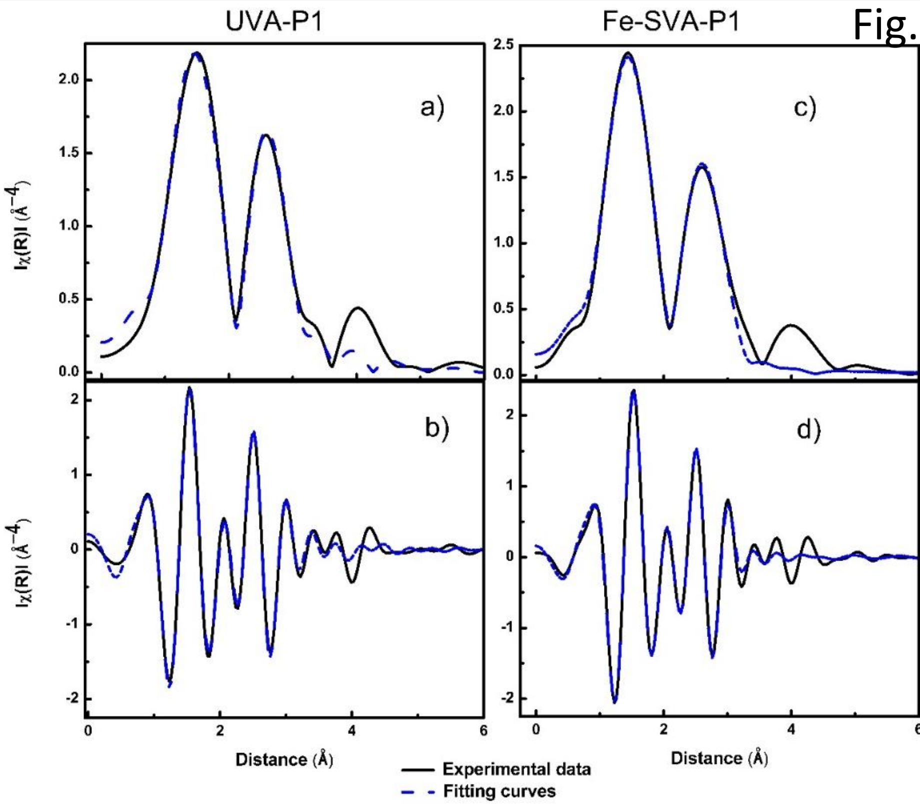
-Calcium selenite ($CaSeO_3$))-wt 54.8(2%);
-Zinc selenide (ZnSe))-wt 32.2(2%);
-Sodium selenite (Na_2SeO_3))-wt 13.(3%)

EXAFS data analysis

- For the EXAFS modelling, least-square fitting based on multiple scattering approximation was employed.
- Single and multiple paths were used.
- The EXAFS theoretical signals for all samples were generated using the FEFF6 code from the backscattering amplitudes and phase shift parameters.
- Knowledge of the space group and crystal structure of the compound to be modelled is required to generate EXAFS theoretical signals.
- Artemis program was used to fit the Fourier transform spectra.
- The R_{factor} parameter which evaluates the difference between the experimental and modelled functions, describes the reliability of the best fit.

V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Fig.19

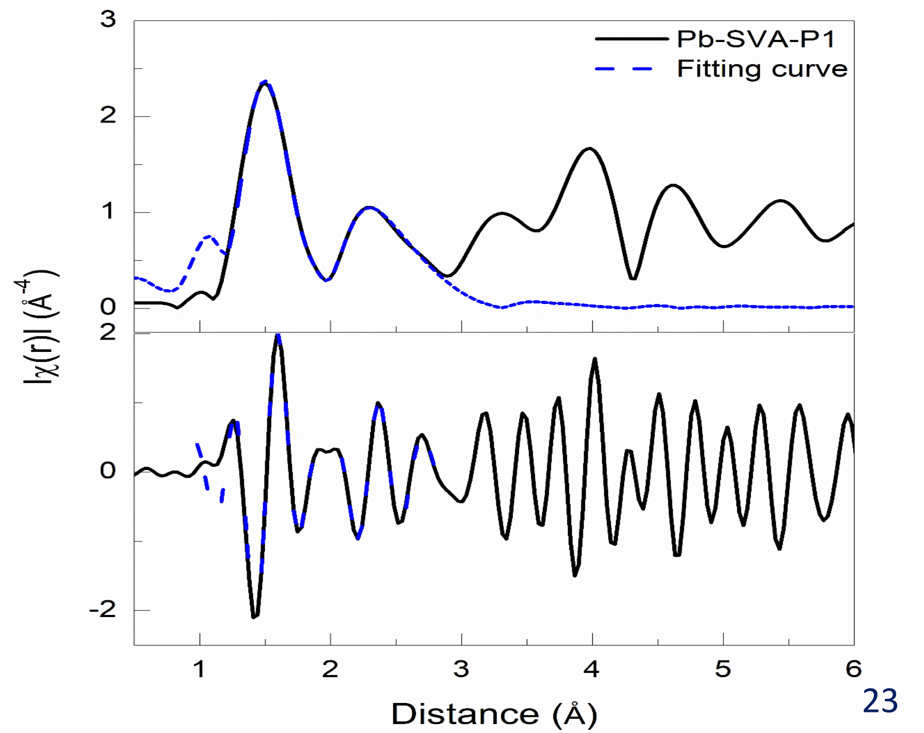


Interaction	CN	R(Å)	σ^2(Å^2)
UVA-P1, ΔE_0 = -4.064 eV, R-factor = 0.002			
Fe-O	3.92± 1.0	2.014±0.006	0.018±0.0003
Fe-Fe	1.65± 0.5	3.008±0.009	0.013±0.0042
Fe-Fe	0.83± 0.3	3.472±0.012	0.023±0.0040
Fe-SVA-P1, ΔE_0 = -2.234 eV, R-factor = 0.006			
Fe-O	3.90± 0.8	2.031±0.002	0.017±0.0004
Fe-Fe	1.97± 0.9	3.032±0.023	0.013±0.0020
Fe-Fe	1.65± 0.9	3.462±0.026	0.030±0.0040

Structural characterization by EXAFS

Standards	Interaction	CN	R(Å)	σ^2(Å^2)
PbO	Pb-O	1.55±0.56	2.000±0.021	0.00909±0.00081
$Pb(C_2H_3O_2)_2$	Pb-O	2.53±0.27	1.7701±0.076	0.04862±0.00694
PbO	Pb-Pb	1.75±0.72	2.2454±0.011	0.00643±0.00086
PbO	Pb-Pb	2.00±0.72	2.8379±0.027	0.02755±0.00842

Fig.20



V-Application of XAS to the characterization of VA sorbed by metals Fe, Pb, Cr, Se

Structural characterization by EXAFS

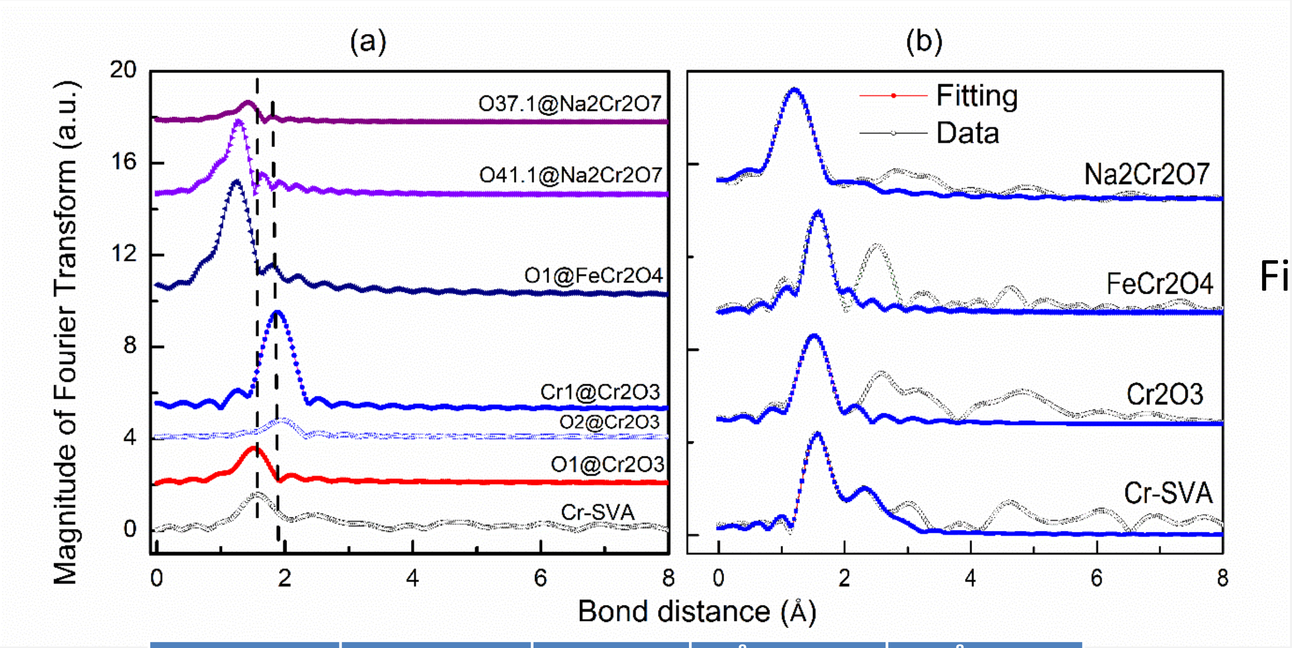


Fig.21

Samples	Interaction	CN	R(Å)	σ^2(Å^2)
Cr-SVA	Cr-O1	3.26(42)	1.69(2)	0.0014(3)
	Cr-O2	2.30(71)	2.59(2)	0.0009(1)
	Cr-Cr1	1*	2.54(2)	0.0023(6)
Cr_2O_3	Cr-O1	4.02(21)	1.79(2)	0.0017(8)
$FeCr_2O_4$	Cr-O1	5.73(58)	1.99(0.7)	0.0004(0.1)
$Na2Cr_2O_7$	Cr-O41.1	3.15(52)	1.67 (3)	0.0065(1)
	Cr-O37.1	1*	1.82(4)	0.0110(3)

For selenium sorbed VA

Ongoing work

Related published papers

1) Lead sorbed onto volcanic ashes investigated by x-ray absorption spectroscopy and complementary techniques, *B.B.B. Njenjock*, ***B. Thiodjio Sendja***, *D. Tchana Kamgne*, *N.A. Medellin Castillo*, *R. Loredo Portales*, *G.J. Labrada Delgado*, *G. Aquilanti*, *G.H. Ben-Bolie*, Journal of Electron Spectroscopy and Related Phenomena 262 (2023) 147268

2) Chemical speciation of lead adsorbed onto volcanic ashes by ICP-OES and XANES, *B.B. Blixen*, ***B. Thiodjio***, *N. Medellin*, *R. Loredo*, *G. Labrada*, *C. Carranza*, *B. Germain*, *R. Leyva, and S. Reyes*, Suplemento de la Revista Mexicana de F´ısica **3** 010602 (2022) 1–8

3) Iron adsorption in Cameroon volcanic ashes insights from x-ray absorption spectroscopy, ***B. Thiodjio Sendja***, *N.A. Medellin Castillo*, *R. Loredo Portales*, *S.T. Kouonang*, *Gladis J. Labrada Delgado*, *C.C. Alvarez*, *L. Olivi*, Physica B 617 (2021) 413128

Conclusion

XAS has been used to characterize the volcanic ash materials tested to adsorb some metal elements.

I- The present study shows that the VA from the CVL of Mount Cameroon volcano can be used as a potential economically sustainable adsorbent for removing pollutants from wastewater.

Reasonable adsorption capacities for Fe, Pb, Cr, Se sorbed by the VA
Adsorption mechanism associated to the ion exchange process

II- XAS might appear as a powerful characterization tool for adsorbent material containing heavy elements. Since it allows determining:

1-Oxidation state of the metal sorbed VA
2-Chemical composition of the metal sorbed VA
3-Structural characterization of the metal sorbed VA

Acknowledgements

National Advanced School of Engineering of Yaounde, University of Yaounde I, Cameroon

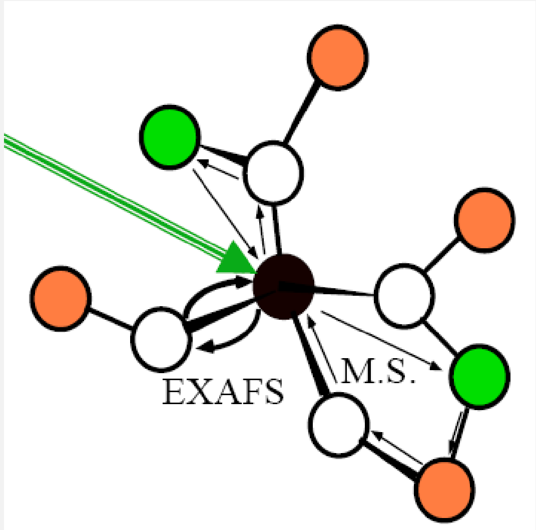
The World Academy of Science (TWAS) + Autonomous University of San Luis Potosi in Mexico

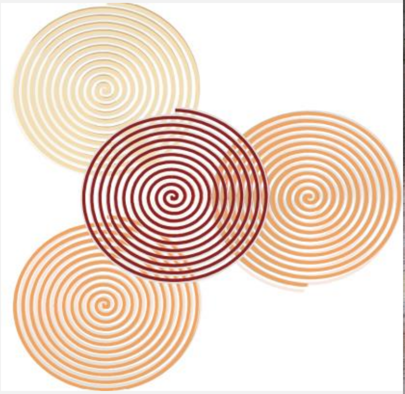
ICTP + ELETTRA: ICTP-ELETTRA users support

LAAAMP Program + ELETTRA

Staff of XAFS beamline ELETTRA

Dr Giuliana Aquilanti, XAFS and XRF beamline scientist





THANK FOR YOUR KIND ATENTION