Hg-Pb binary heavy metals interaction study with Humic Acid: monitoring by FTIR spectroscopy

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Abstract: This work shows that infrared spectroscopy is an easy and fast analytical technique for monitoring the behavior of the humic acids Fluka and Leonardite in contact with binary solutions of mercury and lead. Given the complexity of the structure of humic acid, the experiments were carried out on simple model molecules. The spectra showed a shift (30 cm⁻¹) of the antisymmetric stretching vibration band from the carboxylate function -COO⁻ from 1590 to 1560 cm⁻¹ for the humic acids Fluka-binary solution interaction. In the case of mercury alone, the shift was of 40 cm⁻¹, it can be seen that this shift has dropped by 10 cm⁻¹, which proves that the cationic exchange becomes more difficult.

We have confirmed that the affinity is due to the ionic radius, the reduction potential and the ionic potential. We reinforced this by a fourth parameter which is the frequency separations between the COO⁻ antisymmetric and symmetric stretches (Δνas-s). We have found that Δνas-s is strongly related to the type of fixed metal. The spectra also showed the variation of the intensity of the C=O elongation vibration band of the carboxylic function -COOH up to 1610 cm⁻¹ for the Leonardite humic acid-binary interaction. The high concentration of the binary solution did not result in the total disappearance of the C=O band as in the Leonardite humic acid-mercury alone interaction study. This proves that some carboxylic sites are not accessible to Hg⁴⁺ ions.

Keywords: Humic acid; Binary Hg-Pb competition; Affinity; FTIR Spectroscopy.

1. Introduction

Soil pollution by heavy metals including mercury and lead may be due to negligence, ignorance of the danger level of pollutants or accident during industrial activities causing ecological damage and pollutes holdings of sites and areas surrounding ¹.

Human action has resulted in increased concentrations of heavy metals in the environment. These high concentrations are of concern because they pose risks to human health, as well as to animals and plants ².

The work published by Nriagu and Pacyna ³ makes it possible to assess at a global level the seriousness of the problem posed by the dispersion of heavy metals in the environment. The amounts of mercury and lead are emitted annually worldwide are destructive to fauna and flora. Are estimated to 16.5 thousand tons for mercury and 1266 thousand tons for the lead.

These toxic substances are trapped by the soil that is considered as a reactor, a receiver, an accumulator and a large filter for any pollution ⁴ ⁵. Currently, it is no longer able to play his role of self-cleaner.

The soil consists of solid elements of mineral and organic nature, including humic acid (HA).

Humic acids are complex and heterogeneous mixtures that can give rise to adsorption, ion exchange or even complex through surface oxidation reduction reactions ⁶. They are involved in the transport of a large number of chemical elements in the form of complexes or colloids. The HA is responsible for binding and metal release and manages mobility and bioavailability of metals ⁷ ⁸.

The HA is the expected result of the slow decomposition of plants and animals as soon as they are buried ⁹ ¹⁰. It is a macromolecule of high molar mass (500-5000g mol⁻¹) ¹¹ of a mixed aliphatic-aromatic structure comprising a large number of hydroxyl functions of phenol, alcohol and carboxylic types. These functional groups give humic substances a powerful complexing power ¹² ¹⁴.

The metal ions can be complexed by various ligands, depending on their mutual affinities. In this case, it is the cation exchange capacity (CEC). In soils, 25 to 95% of CEC is found in the organic matter; it is of the order of 150 to 350 meq/100g of HA ¹⁵.

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Recent research showed that the HA could easily capture the mercury only by ion exchange. Several parameters influencing the HA-Metal interaction of which the most important are: the pH, the nature of organic compounds, the ionic strength, and the temperature. Therefore, the study of HA–metal interaction (alone) has become the concern of many works by chemical, physicochemical methods and applied physics to identify, evaluate pollutants and possibly to eliminate these metals. This type of study is based on the coefficient distribution, and adsorption levels are up and the equilibrium constant. This equilibrium is not always achieved because these reactions in the environment are in a continuous state of change to the dynamic process. In nature, several heavy metals may be available at the same time in soils. Therefore, the evaluation of adsorption simultaneous of these cations by the organic matter is very important. For two decades, it was found that many studies focused on the follow-up of the metal competition to be adsorbed on the organic matter of the soil.

Nevertheless, the participation of mercury in the competition with lead alone and Fluka humic acid (FHA) or Leonardite humic acid (LHA) is relatively absent. From Table 1, it is seen that Pb is the most favorable divalent metal to bind to the macromolecule organics. There is significant sorption between Hg and Pb and HA. The objective of our work is to study the competition of Hg and Pb on HA on the one hand and to follow the behavior of the latter in a binary Hg-Pb mixture.

Given the complexity of the structure of humic acids, it was forced to do a study on model molecules. The latter are not representative of the functional groups of humic acid because of its highly complex structure, but they represent distinct classes of the exchange sites, with a binding affinity that can be similar. The molecules we selected for this study of HA-binary interaction (Hg, Pb) are benzoic acid, catechol and salicylic acid.

In order to get closer to the complex structure to the complex structure of humic acid, we have added two other model molecules containing three aromatic rings; it is Xanthene 9-carboxylic acid and Anthralin. In the case of artificial pollution close to the reality, we first used humic acid purchased from the Fluka Company (FHA) and secondly, the humic acid from the International Society of Humid Substances (LHA) also called Leonardite. The HA–Metals interaction was followed firstly by the non-imposed pH before and after the HA-binary mixture (Hg, Pb) and secondly by Infrared Spectroscopy Fourier transformed FTIR.

The studies are focusing on competition focus on metals that have a difference in affinity for humic acid. No study has been carried out on the competition between humic acid and the bivalent heavy metals Hg and Pb, which have a high affinity with humic acid as it is mentioned in Table 1. Besides, the main objective of this work is the analysis of metals combined with humic acid by infrared spectroscopy, which is usually done by atomic absorption and/or plasma torch.

Table 1. Adsorption competition between different divalent cations.

| Source                     | Adsorbant materials       | Ranking in descending order |
|----------------------------|----------------------------|-----------------------------|
| X. Jin et al.              | Humic Substances          | Cr >> Pb > Cu=Ag=Cd=Co=Li   |
| X. Jin et al.              | Peat                      | Cr>Pb>Cu>Ag>Cd=Co=Li        |
| A. Liu et al.              | Purified Humic Acid       | Pb>Cu>Cd                    |
| J. C. Echeverria et al.    | Basic and Acid Sol        | Pb>Cu>Ni>Cd>Zn              |
| E. F. Covelo et al.        | Humic Umbrisol            | Pb>Cr>Cu>Cd~Ni~Zn           |
| C. Plaza et al.            | Humic Acids               | Pb>Cu>Cd>Zn                 |
| P. Janos et al.            | Untreated Low-Rank Coal   | Pb>Cu>Cd>Zn> Ni>Co          |

The FTIR spectroscopy technique is a fast and simple technique. It can provide considerable insight into the structural arrangement of oxygen and carbon in humic acids. The results of the infrared study were confirmed by the ICP-AES analyzes of the metal cation exchanged.

2. Materials and Methods

2.1. Interaction model molecules - binary (Hg, Pb)

The model molecules that we adopted were chosen based on the results of Shulten and Shnitzer which showed that HA is a complex macromolecule containing several aromatic rings which carry carboxylic and salicylic functions while the phenolic functions are grafted on the aliphatic chains. N and S elements, although they also play a significant role in the interaction with heavy metals, were not included in our models.

Our choice fell on two series: The 1st is composed of a single aromatic ring (benzoic acid, catechol and salicylic acid; from Merck). The 2nd is composed of three aromatic rings (Xanthene 9-carboxylic acid and Anthralin; from Aldrich). The developed formulas of the model molecules are shown schematically in Fig.1.
Benzoic acid  
Catechol  
Salicylic acid  

Anthralin  
Xanthene 9-carboxylic acid  

Figure 1. Schematic representation of the developed formula of the model molecules

For all these model molecules, the preparation of the mercury and lead salts was done in the same way according to the following procedure: one gram of each model compound in its acid form is neutralized with NaOH (2M) to which is added either a solution of mercury acetate (1M: from Fluka) or lead nitrate (1M: Fluka) or a mixture of both solutions (Binary). The addition of each solution allowed the precipitation (white solid) of the carboxylate and phenolate of mercury and lead. These salts were then studied by FTIR spectroscopy and compared to their acid form. Two milligrams of each precipitate was dried at 80°C and milled in 100 mg of anhydrous KBr. The powder obtained was placed in a mold to be pelletized and subjected to a pressure of 9.81 x10^6 Pa. The pellet of 13 mm diameter was analyzed directly by FTIR spectroscopy. The spectrometer used is a Bruker YEWS 48. We worked in the range 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹.

2.2. Characterization of humic acids

The commercial humic acid studied comes from the company Fluka (FHA) (45729/150300). FHA has been used in salt form as a model of HA of soil 35. The second humic acid used is the Leonardite (LHA) provided by the International Humic Substances Society (IHSS) (North Dakota, USA). It was isolated by IHSS protocol 36. Chemical and spectroscopic FTIR analyzes were used to characterize the studied humic acids:

(i) Basic tests to detect C, H, N, S and O present in the AHF by CHNS elemental analyzer LECO type (Laboratory Equipment Corporation) Model 932. This apparatus uses samples of the order of 2 to 5 mg. The elementary compositions of LHA were performed by Huffman Laboratories, Inc., Wheatridge, CO.

(ii) The analysis of the acidity of the carboxylic functions was carried out by the calcium acetate technique as well as the determination of the total acidity by barium hydroxide 41,42. Each analysis was repeated three times;

(iii) The analysis of metals (Na, Ca, Fe, Mg, Si and Al) commonly found in FHA and LHA in addition to mercury and lead was carried out by ICP-AES (Varian, axial view, liberty series V);

(iv) The calculation of ash was determined in our previous works 36,35;

(v) Humic acids FHA and LHA were analyzed by FTIR spectrometry before interaction with the same solution of mercury or lead. We used pelletizing technique with KBr in the study of model molecules.

2.3. Interaction Humic acid–binary (Hg, Pb)

200 mg of Humic Acid (FHA or LHA) were added to 50 ml of the solution of Milli-Q water. The procedure of humic acid interaction with mercury and lead mixed solution is the same. Mercury solutions were obtained from mercury acetate solutions Hg(CH₃COO)_2 with concentrations of 0.1, 0.5 and 1.0 g L⁻¹.

Lead solutions were prepared from lead nitrate Pb(NO₃)₂ at the concentrations of 0.1, 0.5 and 1.0 g L⁻¹. Three binary systems (Hg, Pb) at three different concentrations were prepared in ratios of 1:1 (0.1; 0.5 and 1 g L⁻¹). 200mg of HA (FHA or LHA) were added to 50 ml of the mixed solution Hg-Pb. Eight samples were thus obtained, including the control.

The initial pH was measured immediately after addition of the solution of mixed or straightforward metal about 200 mg of HA. The final pH was measured after 24 hours of stirring time. This is followed by centrifugation of 2400 tr.min⁻¹ for 1 hour. The solid parts (HA + metals fixed) are dried at 80°C during 16H. After drying, the solid parts can be analyzed by FTIR spectroscopy. The recovered supernatants are determined by ICP-AES to determine the remaining amounts of mercury and lead metal and other mineral elements Na, Ca, Fe, Mg, Si and Al. All experiments were repeated three times at the same temperature of 25°C.
3. Results and discussion

3.1. FTIR analyses of the interaction model molecules-metal single and binary

3.1.1. Molecules models composed of a single aromatic ring

The FTIR spectra show the strong polarity of the C=O bond of the -COOH function, which makes it very intense and therefore very recognizable. The vibration of elongations $\nu_{C=O}$ corresponding appears between 1716 and 1650 cm$^{-1}$. While the $\nu_{C=O}$ elongation vibrations of the acid function are observed between 1300-1230 cm$^{-1}$, the hydroxyl forms are assigned to large bands in 3400-3200 cm$^{-1}$ range, due to O-H stretching. The other characteristic bands are O-H deformation vibrations of phenol or alcohol type in 1370-1350 cm$^{-1}$ range (Table. 2).
The interaction of the model molecules with the heavy metals Hg, Pb or binary Hg-Pb caused the displacement of the characteristic peaks of the carboxylate function according to the corresponding metal ion. Indeed, the frequency of the $v_{as}$ changes from 1593 to 1496 cm$^{-1}$ and that of the $v_s$ varies from 1390 to 1361 cm$^{-1}$. This shift was confirmed by the calculation of frequency separations $\Delta v_{as-s}$ between the $v_{as}$ and $v_s$.

### 3.1.1.1. Benzoic acid and salts

The FTIR spectra of benzoic acid and their metal salts presented in Fig.2a shows the main characteristic attributions of the carboxylic function and carboxylate. The attributions are summarized in Table 2. The vibration elongations C=O and C-O of the COOH function were observed respectively at 1676 and 1230 cm$^{-1}$. There is also a large band $v_{OH}$ of acids between 3200-2500 cm$^{-1}$. For the benzoic spectra of the salified acid (Hg, Hg-Pb, Pb), we observed two significant changes in comparison with the spectrum of benzoic acid: disappearance of the bands $v_{OH}$, $v_{C=O}$ and $v_{CO}$ characteristics of carboxylic functions –COOH in favor of the appearance of two elongation vibration bands characteristics of the carboxyl functions ate –COOM which are:

(i) The $v_{C=O}$ symmetrical ($v_s$) at 1390 cm$^{-1}$ for the mercury salt at 1308 cm$^{-1}$ for the binary salt and 1365 cm$^{-1}$ for the lead salt,

(ii) The $v_{C=O}$ antisymmetric ($v_{as}$) at 1496 cm$^{-1}$ for the mercury salt and at 1498 cm$^{-1}$ for the binary salt and 1500 cm$^{-1}$ for the lead salt.

After the interaction of benzoic acid with metal solutions, symmetric C-O peak shift to large wavenumbers and asymmetric $v_{C=O}$ peak shift towards low wavenumbers were observed. This shift in the case of mercury alone was higher than for lead alone. Thus values of $\Delta v_{as-s}$ for the salts of Hg and Hg-Pb binary and Pb are of 16, 118 and 135 cm$^{-1}$, respectively (Table 2). The benzoic acid thus has an affinity with mercury relative to the lead. This affinity was disrupted by the presence of mercury and lead as the displacement was reduced.

### 3.1.1.2. Salicylic acid and salts

FTIR spectra of salicylic acid and its salts of mercury, binary (mercury, lead) and lead (Fig.2b) show that the two elongation frequencies of the function –COOH ($v_{C=O}$) at 1658 cm$^{-1}$ and $v_{C=O}$ at 1249 cm$^{-1}$ have been replaced by those of $v_{as}$ of the function -COO$^-$ at 1554 cm$^{-1}$ for the mercury salt, at 1565 cm$^{-1}$ for the binary and 1593 cm$^{-1}$ for the lead salt. Vibration $v_{OH}$ of the same function -COO$^-$ appears at 1384 cm$^{-1}$ for the mercuric salicylate at 1375 cm$^{-1}$ for binary salicylate and 1361 cm$^{-1}$ for lead salicylate (Table 2). There is an important shift of $v_s$ and $v_{as}$ for the case of the salicylic acid-mercury interaction alone indicating the power of mercury in front of lead alone. This affinity was slowed in the presence of mercury and lead since the shift of the elongation peak $v_{as}$ and $v_s$ has decreased with 10 cm$^{-1}$. This diminution is caused by the increase of the $\Delta v_{as-s}$ (170 cm$^{-1}$) for the Hg salt at 190 cm$^{-1}$ in the binary Hg-Pb salt. If we compare the FTIR spectra of salicylic acid and its metal salts studied, we can see the complete disappearance of the $v_{OH}$ stretching frequencies observed between 3400-3200 cm$^{-1}$ and the deformation $\delta_{OH}$ at 1380 cm$^{-1}$. 

**Figure 3.** FTIR spectra of model molecules with three aromatic rings before and after interaction with mercury and lead: (a) Xanthene 9 Carboxylic Acid and (b) Anthralin.
Table 2. Assigning bands of the main functions of model molecules before and after interaction with Hg, Pb and binary (Hg-Pb).

| Vibration of the function | -COOH | -OH | -COO | C=O | C- O-C | References |
|---------------------------|-------|-----|------|-----|--------|------------|
| **Unit**                  | cm⁻¹  | cm⁻¹| cm⁻¹ | cm⁻¹| cm⁻¹   |            |
| Benzoic acid              | 1676  | 1230| 2500-3200 | -  | -      | -          | M. C. Terkhi et al. 16 |
| Benzoic acid + Hg²⁺       | -     | -   | (-) a | -  | 1496  | 1390  | 106 | - | - | - | M. C. Terkhi et al. 16 |
| Benzoic acid + Binary (Hg²⁺,Pb²⁺) | - | - | (-) a | -  | 1498  | 1380  | 118 | - | - | - | This study |
| Benzoic acid + Pb²⁺       | -     | -   | (-) a | -  | 1500  | 1365  | 135 | - | - | - | P. Gossart et al. 35 |
| Catechol                  | -     | -   | 3442-3318 | 1359 | -     | -      | - | - | - | - | M. C. Terkhi et al. 16 |
| Catechol + Hg²⁺           | -     | -   | (-) a | (-) a | -     | -      | - | - | - | - | M. C. Terkhi et al. 16 |
| Catechol + Binary (Hg²⁺,Pb²⁺) | - | - | (-) a | (-) a | -     | -      | - | - | - | - | This study |
| Catechol + Pb²⁺           | -     | -   | (-) a | (-) a | -     | -      | - | - | - | - | P. Gossart et al. 35 |
| Salicylic acid            | 1658  | 1249| 3200-3400 | 1380 | -     | -      | - | - | - | - | M. C. Terkhi et al. 16 |
| Salicylic acid + Hg²⁺     | -     | -   | (-) a | (-) a | 1554  | 1384  | 170 | - | - | - | M. C. Terkhi et al. 16 |
| Salicylic acid + Binary (Hg²⁺,Pb²⁺) | - | - | (-) a | (-) a | 1565  | 1375  | 190 | - | - | - | This study |
| Salicylic acid + Pb²⁺     | -     | -   | (-) a | (-) a | 1593  | 1361  | 232 | - | - | - | This study |
| Xanthène 9 Carboxylic Acid| 1670  | 1233| 2900-3300 | -  | -      | -      | - | 1233 | 1030 | This study |
| Xanthène 9 Carboxylic Acid + Hg²⁺ | - | - | (-) a | -  | 1500  | 1383  | 117 | - | 1236 | 1030 | This study |
| Xanthène 9 Carboxylic Acid + Binary (Hg²⁺,Pb²⁺) | - | - | (-) a | -  | 1513  | 1374  | 139 | - | 1233 | 1030 | This study |
| Xanthène 9 Carboxylic Acid+ Pb²⁺ | - | - | (-) a | -  | 1585  | 1308  | 277 | - | 1235 | 1030 | This study |
| Anthrakin                 | -     | -   | 2950-3100 | 1330 | -     | -      | - | 1604 | - | - | This study |
| Anthrakin + Hg²⁺          | -     | -   | (-) a | (-) a | -     | -      | - | 1601 | - | - | This study |
| Anthrakin + Binary (Hg²⁺,Pb²⁺) | - | - | (-) a | (-) a | -     | -      | - | 1601 | - | - | This study |
| Anthrakin + Pb²⁺          | -     | -   | (-) a | (-) a | -     | -      | - | 1603 | - | - | This study |

a Disappearance
3.1.1.3. Catechol and salts
The FTIR spectrum catechol shown in Fig. 2c indicates the presence of the hydroxyl function characterized by two major bands. The first is the \( \delta_{\text{OH}} \) bending vibration at 1359 cm\(^{-1}\), the second has \( \nu_{\text{OH}} \) stretching frequency at 3442 cm\(^{-1}\) and 3318 cm\(^{-1}\). The catechol-metal interaction (single or binary) has removed the two characteristic bands of the phenol form.

3.1.2. Model molecules with three aromatic rings
3.1.2.1. Xanthene 9 carboxylic acid and salts
The FTIR spectrum of xanthene 9 carboxylic acid (Fig. 3a) shows the corresponding adsorption band to the \(-\text{COOH}\) function which appears at 1670 cm\(^{-1}\) for the elongation vibration \( \nu_{\text{C-O}} \). While the stretching vibration \( \nu_{\text{C=O}} \) of the same acid function is observed strongly at 1233 cm\(^{-1}\) (Table 2) which may also be characteristic of the \( \nu_{\text{C=O}} \) asymmetric (\( \nu_{\text{as}} \)) of the ether function C=O-C. On the other hand, the \( \nu_{\text{C-O}} \) symmetric (\( \nu_{\text{s}} \)) of the ether function C-O-C is observed weakly at 1030 cm\(^{-1}\). The FTIR spectrum of xanthene 9 carboxylic acid also shows an absorption band corresponding to the OH function that appears between 2900 and 3300 cm\(^{-1}\) presented in the form of a wide band.

After the fixation of Hg, Pb and the binary Hg-Pb, we have noticed: (i) the disappearance of the bands of the carboxylic and hydroxyl functional groups and (ii) the shifts of the antisymmetric elongation bands \( \nu_{\text{as}} \) - COO\(^{-}\) to the low frequencies corresponding to the salts of mercury, binary Hg-Pb and lead. They are observed respectively at 1500, 1513 and 1585 cm\(^{-1}\) (Table. 2). The symmetrical elongations \( \nu_{\text{s}} \) of - COO\(^{-}\) are attributed to 1383, 1374 and 1308 cm\(^{-1}\) bands. These shifts show that mercury was able to easily form complexes compared to lead. Indeed, the peak characteristic of \( \nu_{\text{as}} \) of -COO\(^{-}\) was displaced by 170 cm\(^{-1}\) for mercury alone. For the binary solution, the shift was of 157 cm\(^{-1}\) and only 85 cm\(^{-1}\) for lead alone. The shifts observed in the pics of \( \nu_{\text{as}} \) and \( \nu_{\text{s}} \) have caused the increase of \( \Delta \nu_{\text{as}} \) of 117 until 227 cm\(^{-1}\) for the Hg and Pb salts, respectively. This is probably due to the interaction between COO\(^{-}\) and Hg\(^{2+}\) which is more important than that between COO\(^{-}\) and Pb\(^{2+}\). It can be seen in Fig.3a that the characteristic bands of the ether function are always present before and after Xanthene 9 carboxylic acid-metal interaction.

3.1.2.2. Anthralin and salts
The FTIR spectra of anthralin and its salt forms are grouped in Fig. 3b and the main frequencies corresponding are summarized in Table 2. We have noted the deformation frequencies \( \delta_{\text{OH}} \) of the OH function at 1330 cm\(^{-1}\), the elongation frequency \( \nu_{\text{OH}} \) of the OH function between 2950-3100 cm\(^{-1}\) and an intense frequency at 1604 cm\(^{-1}\) which corresponds to the elongation vibrations \( \nu_{\text{C-O}} \) of the function \(-\text{C}=\text{O}\). The interaction with the mercury, lead, and the binary Hg-Pb results to the formation of anthralin which the elongation characteristic band \( \nu_{\text{C-O}} \) and the deformation \( \delta_{\text{OH}} \) disappear completely. On the other hand, the characteristic peak of the C=O function has not varied.

3.2. Summary analyses by FTIR
These model molecules do not make possible the characterization of a real behavior between the macromolecule of humic acid type and heavy metals. The study of these models has validated, on the one hand, the use of FTIR for a specific type of interaction and, on the other hand, to help the characterization with a systematic interpretation of FTIR spectra of more complex molecules. Indeed, the FTIR spectra (Figs.2 and 3) show two main behaviors during the study of the interaction of model metal molecules (single or binary):

(i) The easy monitoring of the frequency band related to the vibration of antisymmetric and symmetric elongation carboxylates in the region 1700 and 1383 cm\(^{-1}\). This frequency depends on the fixed metal cation.\(^{44,46}\) We noted for model molecules with carboxylic functions, that the wavenumbers of antisymmetric vibrations \( \nu_{\text{as}} \) (COO\(^{-}\)) of Hg are lower than those of the binary (Hg, Pb) and Pb alone. While the \( \nu_{\text{s}} \) frequency of the Hg salt is higher than the Hg-Pb binary and Pb salts frequencies.

This suggests that mercury alone is easily attached to the COOH functional sites of the model under study. These frequencies are disturbed by the presence of lead which is probably due to the competition between these two metals to occupy these functional carboxylic sites. Liu et al.\(^{47}\) found similar results when studying the interaction of peat with mixed solutions of Cu, Ni and Cd. They attributed this competition to the repulsive electrostatic forces.

(ii) In the case of the interaction of the model molecule which contains only an OH function with the single or binary metal, in both cases, the disappearance of the characteristic bands of the hydroxyl function was observed. Inhibition of mercury binding in the presence of lead was not visible in the FTIR spectra (Figs.2 and 3). In previous work, Bosire et al.\(^{48}\) confirmed the vital role of acidic functions in forming bonds with Pb, Cu and Zn. Phenol sites were the least likely to be involved in this link because their acidity constants were low.

Our study by FTIR spectroscopy has the advantage of easily following the evolution of the characteristic bands of antisymmetric elongations \( \nu_{\text{as}} \) of symmetric elongations \( \nu_{\text{s}} \)and of the Carboxylate function and \( \nu_{\text{C-O}} \) of the carboxylic function to study the interactions between FHA, LHA and heavy metals.
3.3. Comparison of the characteristics of the studied humic acids
3.3.1. Elementary, ash content results, functional group and ICP-AES determination

Elementary analysis of C, H, N, S and O (Table 3) showed results closer values announced by Steelink. The oxygen level is still relatively high for FHA; it is well above the range of 32.8-38.3% usually found.

Table 3. Elemental, ash content results and acidity analysis of used humic acid.

| Humic acid | FHA | LHA | Reference |
|------------|-----|-----|-----------|
| C          | 44.94 | 63.25 | C. Steelink 11 |
| H          | 3.84  | 3.64  | 3.2-6.2    |
| N          | 0.75  | 1.17  | 0.8-4.3    |
| S          | 1.10  | 0.84  | 0.1-1.5    |
| O          | 49.35 | 31.05 | 32.8-38.3  |
| C/N        | 59.92 | 54.06 | -          |
| C/H        | 11.70 | 17.37 | -          |
| C/O        | 0.91  | 2.03  | -          |
| Ash content b,c | 19.7 | 2.58  | -          |
| Total acidity d | 4.62 | 7.10  | -          |
| R-COOH d   | 4.20  | 6.84  | -          |
| R-OH d     | 0.42  | 0.26  | -          |

| Humic acid | FHA | LHA | Reference |
|------------|-----|-----|-----------|
| R-COOH d   | 4.20 | 6.84 | -         |
| R-OH d     | 0.42 | 0.26 | -         |

Table 4 also shows that FHA contains almost 100 times the amount of Si as LHA and 2 times more aluminum than LHA. This shows the presence of the mineral part as an impurity such as SiO₂, Al₂O₃ and Fe₂O₃. The ash content of 19.7% in FHA confirms the presence of these oxides. The amounts of oxygen in LHA are lower than those of FHA. This is because LHA is pure, contains significantly less iron, aluminum or silicon oxides.

Similarly, the carbon content in FHA is well below the range of 53.8-58.7%, and the nitrogen percentage is 0.75%. Thus, LHA contains more carbon (63.25%) and more nitrogen (1.17%) than FHA. Following the results of the elementary analysis, the variation of the C/N ratios is obtained in the following order: LHA < FHA (54.06 < 59.92). These values reflect significant incorporation of nitrogen compounds in LHA. The C/O ratios vary according to the following sequence: FHA < LHA (0.91 < 2.03). These values reflect the level of oxygenated functional groups of each of these compounds, which is explained by the fact that LHA contains significantly fewer iron, aluminum or silicon oxides. In parallel, the ICP-AES quantitative analysis of the two humic acids (Table 4) proves the purity of LHA and the sodium salt and calcium form of FHA. In fact, it contains an FHA does a significant amount of Na and Ca, of the order of 36800 and 21800 mg Kg⁻¹ respectively while LHA has only 2000 mg Kg⁻¹ of Na and 3000 mg Kg⁻¹ of Ca.

The results of the total acidity and the content of carboxylic groups for humic acids (FHA, LHA) are grouped in Table 4. The results of the carboxylic and phenolic functional determinations for FHA are respectively of the order of 4.20 and 0.26 mol kg⁻¹. The total acidity is estimated at 4.62 mol kg⁻¹. The data in Table 4 also indicate that LHA is more acidic than FHA. The total acidity content in LHA was almost twice that of FHA. A possible explanation for the different elemental composition for the two humic acids can be found in their precursor materials and the influence of climatic conditions during the humification process.
Table 4. Cations titration of the studied HA. The sorption HA-mercury (1.0 g L\(^{-1}\)) and the sorption HA-lead (1.0 g L\(^{-1}\)) and the sorption HA-Binary (mercury-lead)(1.0 g L\(^{-1}\)).

| Reference | P. Gossart et al. \(35\) | M. C. Terkhi et al. \(16\) | This study | This study |
|-----------|-------------------------|-------------------------|------------|------------|
| FHA       | 0g L\(^{-1}\)          | Hg (1.0 g L\(^{-1}\))  | Pb (1.0 g L\(^{-1}\)) | (Hg-Pb) (1.0 g L\(^{-1}\)) |
| Na (mg Kg\(^{-1}\)) | 36800         | 2000             | 2900        | 2500       |
| Ca (mg Kg\(^{-1}\)) | 21800         | 7600             | 8500        | 8050       |
| Fe (mg Kg\(^{-1}\)) | 13800         | 11000            | 12500       | 11750      |
| Mg (mg Kg\(^{-1}\)) | 4400          | 1500             | 2100        | 1800       |
| Hg (mg Kg\(^{-1}\)) | 0            | 248750           | 0           | 112500     |
| Pb (mg Kg\(^{-1}\)) | 60           | 60               | 240000      | 103750     |
| Si (mg Kg\(^{-1}\)) | 18000         | 15000            | 16000       | 15600      |
| Al (mg Kg\(^{-1}\)) | 9000          | 6500             | 7200        | 6900       |

| Reference | P. Gossart et al. \(35\) | M. C. Terkhi et al. \(16\) | P. Gossart et al. \(35\) | This study |
|-----------|-------------------------|-------------------------|-------------------------|------------|
| FHA       | 0g L\(^{-1}\)          | Hg (1.0 g L\(^{-1}\))  | Pb (1.0 g L\(^{-1}\))  | (Hg-Pb) (1.0 g L\(^{-1}\)) |
| Na (mg Kg\(^{-1}\)) | 2000         | 170               | 200         | 185        |
| Ca (mg Kg\(^{-1}\)) | 3000         | 0                | 0           | 0          |
| Fe (mg Kg\(^{-1}\)) | 2000         | 995              | 1075        | 1035       |
| Mg (mg Kg\(^{-1}\)) | 40           | 0                | 0           | 0          |
| Hg (mg Kg\(^{-1}\)) | 0            | 175000           | 0           | 78750      |
| Pb (mg Kg\(^{-1}\)) | 65           | 65               | 104500      | 43750      |
| Si (mg Kg\(^{-1}\)) | 150          | <150             | <150        | <150       |
| Al (mg Kg\(^{-1}\)) | 2500         | <2500            | <2500       | <2500      |

3.3.2. Vibrational characteristics

The analysis of the infrared spectra of the FHA and LHA humic acids are shown in Fig. 4. The two spectra obtained have great similarities for the general appearance and the positions of the main peaks. FTIR spectra can be divided into two main regions \(30,51\). The first region (4000-1900 cm\(^{-1}\)) is similar for FHA and LHA. It contains broad peaks characteristic of humic substances. They are attributed mainly to the elongation vibration \(\nu_{\text{O-H}}\) and \(\nu_{\text{N-H}}\). Between 3450 and 3300 cm\(^{-1}\), phenol -OH elongation bands of hydrogen bonds can be observed. Between 2965 and 2840 cm\(^{-1}\), the spectra of the two acids show very weak vibration bands characteristic of the C-H aliphatic bond constituting -CH\(_2\) and -CH\(_3\). In the second region (1900-400 cm\(^{-1}\)), the FHA and LHA FTIR spectra change significantly and confirm the salt (impure) form of FHA and the (pure) acid form of LHA already found by elementary ICP-AES and functional group dosage.
Table 5 summarizes the main results in the characterization of the humic acids studied. The presence of the band corresponding to the extension of the \( \text{C} = \text{O} \) bond of the strong carboxylic acids to 1709 cm\(^{-1}\) of LHA indicates its purity. However, it is absent in the spectrum of FHA, thus confirming its salt form. The characteristic asymmetric elongation band \( \nu_{\text{as}}\text{-COO} \) appears at 1590 cm\(^{-1}\). The characteristic symmetric elongation band \( \nu_{\text{s}}\text{-COO} \) appears at 1386 cm\(^{-1}\). The spectrum of FHA (Fig. 4a) shows the Si-O elongation vibration band of silica located around 1031 cm\(^{-1}\), indicating the presence of the mineral part \(^{33}\) (Table 5).

This band is no longer visible in the case of LHA (Fig. 4b) proving that it consists mainly of organic matter. This spectral information will be useful for the study of the behavior of organic matter (LHA) when interacting with metallic elements and observing their spectral changes. It should be noted that the mineral part of soils also has a high adsorption capacity of metals. Indeed, Babel et al. have shown the existence of a low-cost inorganic or organic adsorbents used for the removal of heavy metals \(^{32}\).

### 3.4. Study of interactions HA-binary (Hg-Pb)\(^a\)

Tables 4 and 6 show the results of the analysis as a function of pH, adsorption percentages, the characteristics of the function -COOH and -COO\(^{-}\) and cation analysis before and after complexation.

#### 3.4.1. Study of interactions FHA-binary (Hg-Pb)\(^a\)

**3.4.1.1. Influence of the concentration of the mixed solution Hg-Pb**

Data from the study of FHA-Metal interactions alone or binary at different concentrations 0.1, 0.5 and 1 g L\(^{-1}\) are grouped in Table 6. The results show that:

(i) For a mixed solution to a concentration of 0.1 g L\(^{-1}\) mercury and 0.1 g L\(^{-1}\) of lead, the fixation percent of mercury and lead was respectively of the order of 89% and 85%.

(ii) When the concentration of mercury and lead increases in the mixture (0.5 g L\(^{-1}\)), the fixation percentage of these metals increase slightly by 3%.

(iii) A concentration of 1 g L\(^{-1}\) of the mixed solution, the percentage of binding is 90% for mercury and 83% for lead.

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**Table 5.** Summary of the main results of the different methods of analysis used in the characterization of the studied humic acids.

| Sample  | Chemical analysis | Acidity | FTIR Spectroscopy | Information obtained |
|---------|------------------|---------|-------------------|---------------------|
|         | C (%) | O (%) | Na (mg Kg\(^{-1}\)) | Ca (mg Kg\(^{-1}\)) | Si (mg Kg\(^{-1}\)) | Ash (%) | R-COOH (%) | \( \nu_{\text{COO}} \) cm\(^{-1}\) | \( \nu_{\text{COO}} \) cm\(^{-1}\) | \( \nu_{\text{O-Si}} \) cm\(^{-1}\) | Forme of sample | Etat of sample |
| FHA     | 44.94 | 49.35 | 36800 | 21800 | 18000 | 19.7 | 4.20 | Absence | 1590 | 1386 | 1031 | Sel | Impure |
| LHA     | 63.25 | 31.05 | 2000 | 150 | 2.58 | 6.84 | 1709 | 1608 | 1429 | Absence | Acide | Pure |
Table 6. Chemical characterization of the sorption HA-mercury, HA-lead and HA-Binary (mercury-lead)

| Humic Acid | Initial Concentration of métal | Adsorption system | Initial pH | Final pH | Mass adsorbed (mg) | % of adsorption | Reference |
|------------|--------------------------------|-------------------|------------|----------|--------------------|-----------------|-----------|
| FHA        | 0 g L\(^{-1}\) | Blank | 4.45 | 6.50 | 0.0 | 0.0 | M. C. Terkhi et al.\(^\text{16}\) |
| FHA        | 0.1 g L\(^{-1}\) | Hg | 5.27 | 6.20 | 4.55 | 91 | M. C. Terkhi et al.\(^\text{16}\) |
| FHA        | 0.1 g L\(^{-1}\) | Pb | 5.25 | 6.18 | 4.50 | 90 | P. Gossart et al.\(^\text{35}\) |
| FHA        | 0.1 g L\(^{-1}\) | Hg (Hg,Pb) | 5.27 | 6.20 | 2.22 | 89 | This study |
| FHA        | 0.1 g L\(^{-1}\) | Pb (Hg,Pb) | 5.27 | 6.20 | 2.12 | 85 | This study |
| FHA        | 0.5 g L\(^{-1}\) | Hg | 5.03 | 5.22 | 23.75 | 95 | M. C. Terkhi et al.\(^\text{16}\) |
| FHA        | 0.5 g L\(^{-1}\) | Pb | 5.05 | 5.19 | 23 | 92 | This study |
| FHA        | 0.5 g L\(^{-1}\) | Hg (Hg,Pb) | 5.00 | 5.16 | 11.37 | 91 | This study |
| FHA        | 0.5 g L\(^{-1}\) | Pb (Hg,Pb) | 5.00 | 5.16 | 11 | 88 | This study |
| FHA        | 1.0 g L\(^{-1}\) | Hg | 4.80 | 4.25 | 49.50 | 99 | M. C. Terkhi et al.\(^\text{16}\) |
| FHA        | 1.0 g L\(^{-1}\) | Pb | 4.86 | 4.21 | 48 | 96 | P. Gossart et al.\(^\text{35}\) |
| FHA        | 1.0 g L\(^{-1}\) | Hg (Hg,Pb) | 4.84 | 4.24 | 22.50 | 90 | This study |
| FHA        | 1.0 g L\(^{-1}\) | Pb (Hg,Pb) | 4.84 | 4.24 | 20.75 | 83 | This study |
| LHA        | 0 g L\(^{-1}\) | Blank | 5.60 | 3.16 | 0.0 | 0.0 | M. C. Terkhi et al.\(^\text{16}\) |
| LHA        | 0.1 g L\(^{-1}\) | Hg | 5.00 | 2.92 | 4.85 | 97 | M. C. Terkhi et al.\(^\text{16}\) |
| LHA        | 0.1 g L\(^{-1}\) | Pb | 5.02 | 2.95 | 4.1 | 96 | P. Gossart et al.\(^\text{35}\) |
| LHA        | 0.1 g L\(^{-1}\) | Hg (Hg,Pb) | 5.00 | 2.93 | 2.37 | 95 | This study |
| LHA        | 0.1 g L\(^{-1}\) | Pb (Hg,Pb) | 5.00 | 2.93 | 2.27 | 91 | This study |
| LHA        | 0.5 g L\(^{-1}\) | Hg | 4.98 | 2.50 | 19 | 75 | M. C. Terkhi et al.\(^\text{16}\) |
| LHA        | 0.5 g L\(^{-1}\) | Pb | 5.00 | 2.57 | 12.8 | 52 | P. Gossart et al.\(^\text{35}\) |
| LHA        | 0.5 g L\(^{-1}\) | Hg (Hg,Pb) | 5.00 | 2.55 | 8.87 | 71 | This study |
| LHA        | 0.5 g L\(^{-1}\) | Pb (Hg,Pb) | 5.00 | 2.55 | 6.25 | 50 | This study |
| LHA        | 1.0 g L\(^{-1}\) | Hg | 4.96 | 2.20 | 35 | 70 | M. C. Terkhi et al.\(^\text{16}\) |
| LHA        | 1.0 g L\(^{-1}\) | Pb | 4.99 | 2.40 | 21 | 42 | P. Gossart et al.\(^\text{35}\) |
| LHA        | 1.0 g L\(^{-1}\) | Hg (Hg,Pb) | 4.98 | 2.29 | 15.75 | 63 | This study |
| LHA        | 1.0 g L\(^{-1}\) | Pb (Hg,Pb) | 4.98 | 2.29 | 8.75 | 35 | This study |
For these three concentrations, it was noted that the fixed quantity in the case of binary Hg-Pb never reached the maximum quantities fixed, as for the case of mercury alone (99%) and lead alone (96%). The active sites FHA are not all available in the case of the binary solution. This is probably due to the competition and the repulsive electrostatic forces between the two ions Hg$^{2+}$ and Pb$^{2+}$. This suggests that the maximum percentage of adsorption in the binary solution follows the following order: Hg (Hg-Pb) > Pb (Hg-Pb).

3.4.1.2 Initial and final pH

The previous sequence was confirmed by pH monitoring (Table 6). Indeed, at the same concentrations of 0.1 g L$^{-1}$ and 0.5 g L$^{-1}$ of mixed mercury and lead solution, the initial pH is always higher than the final pH. The increase in the final pH is due to the release of the Na$^+$ and Ca$^{2+}$ ions present in the AHF during the exchange with the metal Hg$^{2+}$ and Pb$^{2+}$ ions (Table 4). This increase was slowed in the case of the binary system Hg-Pb.

The study of FHA interactions with individual or mixed solutions at high concentration (1 g L$^{-1}$) showed that the initial pH is always lower than the final pH. It has been concluded that this ion exchange goes through two stages, the first between the Na$^+$ and Ca$^{2+}$ cations, FHA carboxylate functions and the two metals (Table 4).

The second is between the protons carboxylic functions and metals once the carboxylic functions were exhausted. The release of protons present in small quantities in FHA was the leading cause of the decrease in pH. In this step, we can say that FHA has undergone a larger fixation. We also noticed that the decrease was considerable in consideration of the FHA interaction with mercury or lead alone for the mixed solution Hg-Pb.

If we take, for example, the fixing of mercury alone (1 g L$^{-1}$) by FHA, we only have Na$^+$ (2000 mg Kg$^{-1}$) and Ca$^{2+}$ (7600 mg Kg$^{-1}$) (Table 4). The pH filled from 4.8 to 4.25 (Table 6). For the mixed solution Hg-Pb, the change of the form -COO-Na or -COO-Ca to the form -COO-Hg became difficult due to the presence of lead. This inhibition phenomenon is demonstrated by the remaining amount of Na$^+$ (2500 mg Kg$^{-1}$) and Ca$^{2+}$ (8050 mg Kg$^{-1}$).

The data in Tables 4 and 6 also showed that the ion exchange between Pb$^{2+}$ and the Na$^+$ and Ca$^{2+}$ ions was disrupted by the presence of mercury in the study of the FHA-binary interaction Hg-Pb. The Na$^+$, Ca$^{2+}$ dosage, final pH and adsorption percentage values were always lower than those of the FHA-Pb interaction.

3.4.1.3 FTIR Spectroscopy monitoring

Examination of the infrared spectra (Fig.5a) of the complex formed by Fluka humic acid and the Hg and Pb mixture showed the same pattern for the ten spectra found. It has been found that:

(i) The intensity of elongation absorption band $\nu_C-O$ at 1695 cm$^{-1}$ of the carboxylic function did not vary after the interaction of FHA (salt form), regardless of the concentrations of the studied solutions (Table 6).

(ii) The shift of the vibration band elongation symmetrical $\nu_C$ is initially located at 1386 cm$^{-1}$ of the carboxylic functions to the longer wavelengths. The shift values are given in Table 6.
Fig. 5. FTIR spectra of humic acids studied before and after interaction with mercury and lead: (a) FHA and (b) LHA.

The differences were of 12 and 16 cm\(^{-1}\) for the concentration of 0.5 and 1 g L\(^{-1}\), respectively. However, for 0.1 g L\(^{-1}\), the shift was of 3 cm\(^{-1}\) equivalents of the shift of the spectrometer resolution.

(iii) The vibration band elongation has symmetrical \(\nu_{as}\) (1590 cm\(^{-1}\)) of the carboxylate functions has been moved to the lowest wavelengths. There was a shift of 8, 20 and 30 cm\(^{-1}\) corresponding to the concentrations of 0.1, 0.5 and 1 g L\(^{-1}\), respectively. These shifts have confirmed previous results from other chemical analysis methods (Tables 4 and 6). The high concentration of 1 g L\(^{-1}\) caused a shift of 30 cm\(^{-1}\), which means that there is an exchange easier between the elements Na\(^+\) and Ca\(^{2+}\) of the carboxylate function and Hg\(^{2+}\) and Pb\(^{2+}\) ions compared to the low concentrations of 0.1 and 0.5 g L\(^{-1}\). In the case of mercury, the shift was of 40 cm\(^{-1}\); we can see that this shift has dropped by 10 cm\(^{-1}\), which proves that the cationic exchange becomes more difficult.

(iv) The \(\Delta \nu_{as}\) calculated values during the interaction of FHA with heavy metals are presented in Table 7. These values vary substantially with the nature of the metallic agent. It was observed that \(\Delta \nu_{as}\) follows the sequence: \(\Delta \nu_{as}\) (FHA-Hg) \(<\Delta \nu_{as}\) (FHA-Pb) \(<\Delta \nu_{as}\) (FHA-Pb), indicating that the interaction between COO\(^-\) and Hg\(^{2+}\) is greater than that between COO\(^-\) and Pb\(^{2+}\).

3.4.2. Study of interactions LHA-binary (Hg-Pb)

3.4.2.1. Influence of the concentration of the mixed solution Hg-Pb

The adsorption rates in the LHA-Hg, LHA-Pb and LHA-Hg-Pb interactions are summarized in Table 6. We noticed that:

(i) At low concentrations (0.1 g L\(^{-1}\)) of the binary solution, there is significant adsorption of 95 and 91% for mercury and lead, respectively.

(ii) At average concentrations (0.5 g L\(^{-1}\)), adsorption rates decreased by almost 3% compared to the study of the (LHA-single metal) interaction.

(iii) At 1 g L\(^{-1}\) of the mixed solution, the adsorption rates are of the order of 63% for mercury and 35% for lead. These values are lower compared to adsorption with FHA and LHA. The main reason for this phenomenon is the acid form of LHA. Cationic exchange, in this case, was complicated because the competition between Hg\(^{2+}\) and Pb\(^{2+}\) was disrupted by the high acidity of LHA.
Table 7. Frequencies, and maximum shift of the -COO\(^-\) symmetric and asymmetric of the HA interaction with Hg, Pb and Binary (Hg-Pb).

| Humic Acid | Concentration Initial of métal | Adsorption system | \(\nu_{\text{as}}\) (-COO\(^-\)) cm\(^{-1}\) | \(\nu_s\) (-COO\(^-\)) cm\(^{-1}\) | \(\Delta\nu_{\text{as}}\) (-COO\(^-\)) cm\(^{-1}\) | Maximum shift from the frequency of (-COO\(^-\)) cm\(^{-1}\) | Intensity of the C=O elongation vibration band of (-COOH) | Reference |
|------------|--------------------------------|-------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------|
| FHA        | 0 g L\(^{-1}\)                | Blank             | 1590                            | 1386                            | 204                             | No variation                     |          | M. C. Terkhi et al.\(^{16}\) |
|            | 0.1 g L\(^{-1}\)              | Hg                | 1580                            | 1390                            | 190                             | No variation                     |          | M. C. Terkhi et al.\(^{16}\) |
|            |                                | Pb                | 1584                            | 1387                            | 197                             | No variation                     |          | P. Gossart et al.\(^{25}\) |
|            |                                | Hg (Hg,Pb)        | 1582                            | 1389                            | 193                             | No variation                     |          | This study                     |
|            |                                | Pb (Hg,Pb)        | 1582                            | 1389                            | 193                             | No variation                     |          | This study                     |
|            | 0.5 g L\(^{-1}\)              | Hg                | 1565                            | 1401                            | 164                             | -40                             | No variation                     |          | This study                     |
|            |                                | Pb                | 1575                            | 1394                            | 181                             | +19                             | No variation                     |          | This study                     |
|            |                                | Hg (Hg,Pb)        | 1570                            | 1398                            | 172                             | No variation                     |          | This study                     |
|            |                                | Pb (Hg,Pb)        | 1570                            | 1398                            | 172                             | No variation                     |          | This study                     |
|            | 1.0 g L\(^{-1}\)              | Hg                | 1550                            | 1405                            | 145                             | No variation                     |          | This study                     |
|            |                                | Pb                | 1566                            | 1397                            | 169                             | No variation                     |          | M. C. Terkhi et al.\(^{16}\) |
|            |                                | Hg (Hg,Pb)        | 1560                            | 1402                            | 158                             | Important decrease               |          | P. Gossart et al.\(^{25}\) |
|            |                                | Pb (Hg,Pb)        | 1560                            | 1402                            | 158                             | Important decrease               |          | This study                     |
|            |                                | LHA               | 1610                            | 1429                            | 181                             | Appearance                       |          | M. C. Terkhi et al.\(^{16}\) |
|            | 0 g L\(^{-1}\)                | Blank             | 1608                            | 1432                            | 176                             | Decrease                        |          | M. C. Terkhi et al.\(^{16}\) |
|            | 0.1 g L\(^{-1}\)              | Hg                | 1607                            | 1429                            | 178                             | Decrease                        |          | P. Gossart et al.\(^{25}\) |
|            |                                | Pb                | 1609                            | 1431                            | 178                             | Decrease                        |          | This study                     |
|            |                                | Hg (Hg,Pb)        | 1609                            | 1431                            | 178                             | Decrease                        |          | This study                     |
|            |                                | Pb (Hg,Pb)        | 1609                            | 1431                            | 178                             | Decrease                        |          | This study                     |
|            | 0.5 g L\(^{-1}\)              | Hg                | 1599                            | 1436                            | 163                             | Important decrease               |          | M. C. Terkhi et al.\(^{16}\) |
|            |                                | Pb                | 1602                            | 1431                            | 171                             | Important decrease               |          | P. Gossart et al.\(^{25}\) |
|            |                                | Hg (Hg,Pb)        | 1601                            | 1433                            | 168                             | Important decrease               |          | This study                     |
|            |                                | Pb (Hg,Pb)        | 1601                            | 1433                            | 168                             | Important decrease               |          | This study                     |
|            | 1.0 g L\(^{-1}\)              | Hg                | 1591                            | 1441                            | 150                             | Important decrease               |          | M. C. Terkhi et al.\(^{16}\) |
|            |                                | Pb                | 1596                            | 1394                            | 202                             | Important decrease               |          | P. Gossart et al.\(^{25}\) |
|            |                                | Hg (Hg,Pb)        | 1598                            | 1439                            | 159                             | Important decrease               |          | This study                     |
|            |                                | Pb (Hg,Pb)        | 1598                            | 1439                            | 159                             | Important decrease               |          | This study                     |
3.4.2.2. Initial and final pH
The values of the initial and final pH of interactions LHA -single metal LHA-binary are given in Table 6. Whatever the pH concentrations at the end of the LHA-metal reaction alone or binary is always acid medium, of the order of 2-3.

3.4.2.3. FTIR Spectroscopy monitoring
The infrared spectra of the complex formed by LHA and the mixture Hg and Pb are shown in Fig.5b. The characteristics of the carboxylic function and the different attributions of bands related to the carboxylate function in LHA are detailed in Table 4. Three principal bands were followed:

(i) The decrease in elongation vibration intensity $v_{C-O}$ at 1709 cm$^{-1}$ of the carboxylic function reflects the increase in adsorbed metals. It can be deduced that the high concentration of the binary component solution (1 g L$^{-1}$) did not cause the total disappearance of this band as in the case of the LHA interaction with the single-component solution Hg (1 g L$^{-1}$).

(ii) The antisymmetric elongation vibration band $v_{as}$ at 1608 cm$^{-1}$ characteristic of the carboxylate function was shifted to the low wavenumber as a function of the increase in the number of metal cations. A small displacement of about 10 cm$^{-1}$ was recorded for the 0.5 and 1 g L$^{-1}$ concentrations of the binary solution Hg-Pb. This small-displacement confirms that the active sites of LHA are not fully complexed.

(iii) The symmetrical elongation vibration band $v_{s}$ characteristic of the carboxylic function was slightly moved for both the 0.1 and 0.5 g L$^{-1}$ concentrations. On the other hand, this shift was of the order of 10 cm$^{-1}$ for 1 g L$^{-1}$.

(iv) The LHA interaction with the Hg solution has caused an important shift of $v_{as}$ and $v_{s}$ pics of 19 and 12 cm$^{-1}$, respectively (Table 7), therefore a shift rate of almost half compared to the FHA-Hg interaction (40 and 19 cm$^{-1}$). This proves that the interaction between FHA-Hg is easier than the interaction between LHA-Hg. The shit values always follow the same order as in the case of the FHA-metal interaction: $\Delta v_{as}$ (LHA-Hg) < $\Delta v_{as}$ (LHA-Hg-Pb) < $\Delta v_{as}$ (LHA-Pb).

3.5. Selective affinity of adsorption of Hg$^{2+}$ and Pb$^{2+}$
The results of this study are consistent with those found by other works 47,53,54. The rate of adsorption decreased in the case of the interaction of the organic matter (humic acid, lignite, etc.) with mixed solutions (binary and tertiary) according to the work conditions:

- Liu et al. 47 have shown that adsorption capacities in the study of the peat-mono-component interaction (Cu$^{2+}$, Ni$^{2+}$ or Cd$^{2+}$) fall with respect to competitive adsorption capacities in peat-multi-component (Cu$^{2+}$, Ni$^{2+}$), (Cu$^{2+}$, Cd$^{2+}$), (Cd$^{2+}$, Ni$^{2+}$) or (Cu$^{2+}$, Ni$^{2+}$, Cd$^{2+}$).

- Zeledon-Toruno et al. 53 have observed a significant reduction in nickel uptake by LHA after the addition of a binary solution containing both metals (Cu$^{2+}$, Ni$^{2+}$).

- Peter et al. 54 concluded that silicate-immobilized humic material has greater selectivity for mercury. The order of affinity in a mixed solution (Hg, Pb, Cu) was classified as follows: Hg (Hg, Pb, Cu) > Pb (Hg, Pb, Cu) > Cu (Hg, Pb, Cu). In general, organic materials have a selective affinity for certain metals. This affinity has been linked to several factors such as electronegativity 35, ionic potential (Z/r) 36, reduction potential 47 and ionic radius 16. Because of the small size of the Hg$^{2+}$ ions (ionic radius, R$_{Hg^{2+}}$ = 0.83 Å), mercury can create a great deal of competition in occupying the active sites of FHA and LHA compared to Pb$^{2+}$ ions (R$_{Pb^{2+}}$ = 1.33 Å). In addition, the degree of association of the humic acids studied with Hg or Pb in the mixed solution is positively correlated with the reduction potential of Hg$^{2+}$ (+0.8 eV) which is greater than that of Pb$^{2+}$ (-0.13 eV). In parallel, mercury has the highest affinity for FHA or LHA because it has an ionic potential greater than that of lead.

4. Conclusions
The study of the interaction between humic acid and metals using the FTIR spectroscopic technique has made possible the characterization of the main functions responsible for this interaction, such as the carboxylic and carboxylate functions. Indeed, it is sufficient to have at the start a humic acid whose FTIR spectra show the antisymmetric $v_{as}$ and the symmetric $v_{s}$ elongations vibration band of -COO$^{-}$ and C=O of the -COOH function. The displacement of $v_{as}$ and $v_{s}$ bands and the decrease of the peak intensity of the COOH function suggest a metal fixation. The frequency separations between the -COO$^{-}$ antisymmetric and symmetric stretches $\Delta v_{as}$ strongly related to the type of fixed metal. The results of this study showed that the high adsorption capacity of humic acids for mercury compared to lead and the adsorption rate of FHA (salt form) is always higher than LHA (acid form). The selective adsorption of mercury as in the literature has been justified by its small ionic radius, high reduction potential and high ionic potential. In this study we have added a fourth parameter $\Delta v_{as}$ and found that: $\Delta v_{as}$ (HA-Hg) < $\Delta v_{as}$ (HA-Hg-Pb) < $\Delta v_{as}$ (HA-Pb).

The elimination rate of Hg$^{2+}$ and Pb$^{2+}$ in the binary case follows this sequence: Hg (Hg-Pb) > Pb (Hg-Pb) due to the competition phenomenon between these two metallic ions, the mercury elimination rate by FHA and LHA has decreased by 10%. This decrease may affect the performance of humic acid cleaning.
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Conflicts of interest

There are no conflicts to declare.

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