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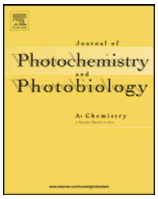

Fourier transform infrared study of mercury interaction with carboxyl groups in humic acids

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ABSTRACT

An interaction between humic acid, an organic part of soil and mercury was studied by Fourier transform infrared spectroscopy (FTIR) and by ICP-AES analysis under given pH and concentration conditions. First the spectroscopic model was validated on the interaction of simple molecules representing the structural components of humic acid such as benzoic acid, catechol and salicylic acid with mercury. The interaction of carboxylic parts of humic acid with mercury is very interesting and easily characterised by infrared spectroscopy, an ideal mean for molecular study. Under the salt form (commercial humic acid Fluka TM: FHA), humic acid reacts with mercury in a different way from its acid form (FHA purified noted PFHA) and the Leonardite (LHA). Because of the straightforward exchange between Na^+, Ca^{2+} and Hg^{2+}, fixation of the latter is much more important with the salt form (FHA). However, this reaction is reduced under the acid form (PFHA, LHA) because the exchange with protons is difficult. The effect of this exchange was studied by FTIR showing the intensity decrease of $\nu_{C=O}$ (—COOH), the carboxylic functional group band of the acid, and the shifting of ν_{as} ($—COO^-$), the carboxylate functional group band under given pH and mercury conditions. For the FHA salt form, the characteristic band $\nu_{C=O}$ (—COOH) represented by a shoulder did not evolute, whereas the corresponding band to ν_{as} ($—COO^-$) strongly shifted ($40\,cm^{-1}$) for a maximum Hg^{2+} concentration ($1\,g\,l^{-1}$). On the other hand, for the acid form (PFHA, LHA), the intense band of $\nu_{C=O}$ (—COOH) disappeared proportionally to the increase of Hg^{2+}concentration and the ν_{as} ($—COO^-$) band moved for about $20\,cm^{-1}$. The same results were reached with pH variations. Our results were confirmed by ICP-AES mercury analysis. This study shows that humic acids react differently according to their chemical and structural state.

1. Introduction

Even though technology and industry are necessary for human welfare, they can seriously harm our environment. Soil pollution by heavy metals is a well known problem threatening nature as well as human health through under soil and surface water contamination [1]. Heavy metals are toxic at tiny amounts. Moreover, our industry contributes indirectly to their concentration on specific sites.

Billions of tonnes of mineral micropollutants are rejected every year. They contaminate the atmosphere (air), the hydrosphere (water) and the lithosphere (soil). They harm seriously the biosphere (living beings). The capacity of soil, a complex medium, to recycle effectively and quickly heavy metals, is under study [2]. For a long time studies were focused on the interaction of metals with clays [3–5]. However, in the last two decades, a special interest was given to the organic part of soil and to its capacity to recycle heavy metals [6–9].

Clays and humic acids represent the major part of soil. Humic acids are natural organic compounds of soil. They result from the decomposition of organic matter. Their structure helps to fix heavy metals, to trap organic molecules and to oxidize or reduce compounds. Humic acid is composed of condensed nuclei related to each other by aliphatic chains (peptides, alkalis) and acid functional groups —COOH and phenolic —OH [10,11]. These two functional groups allow two types of interactions with heavy metals: carboxylate-metal cation and phenolate-metal cation [12–14]. If the interactions with metal are infrared exploited, it is not the same case with the phenol —OH function. The latter possesses a large band practically not exploitable [12,13]. Former work [15–18] and mainly work of Gossart et al. [17,19] showed that the interaction of the HA with Pb^{2+}, Cd^{2+} and Zn^{2+} involves structural variations which can be followed by Fourier transform infrared (FTIR). We consequently carried out our work on the interactions of the humic acid with mercury in order to gather data for deeper soil investigations.

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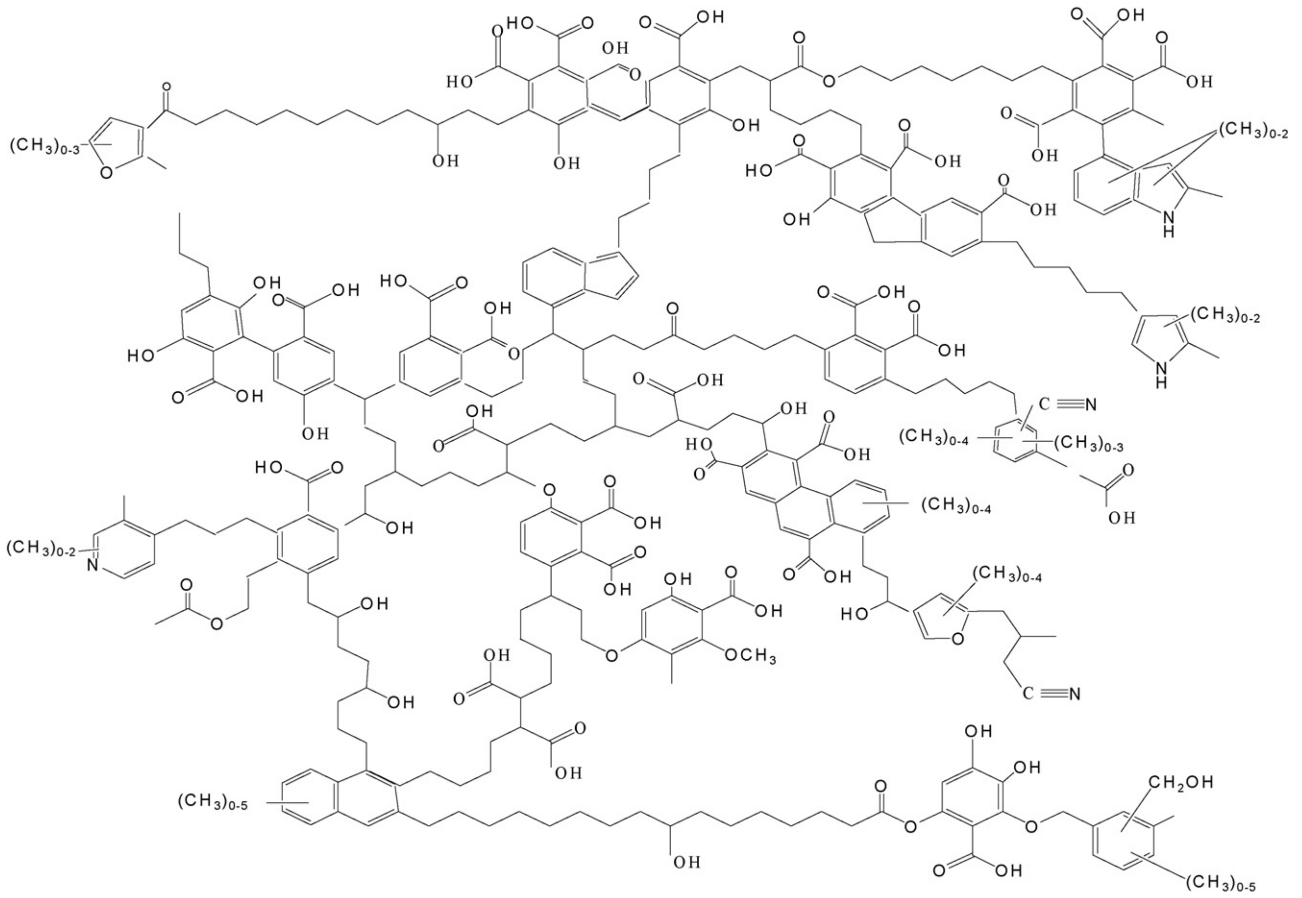

Fig. 1. Humic acid structure as proposed by Schulten and Schnitzer.

We carried out our study in a similar way than in previous works [17,19]: (i) study of the interactions model molecules–mercury for validation of the protocol and (ii) FTIR study of the interaction humic acid (HA)–mercuric ions (Hg^{2+}) under given conditions of pH and concentration [19]. HgO and Hg^{2+} are the most frequent states of mercury oxidation in the soil. The mercury contained in the soil is quickly immobilized in the form of carbonate or phosphate. It is fixed by oxide of iron, manganese and aluminium, [20–22] and especially by organic matter to which, it binds in the form of very stable organometallic complexes [23]. Structural data concerning humic acids is scarce. Nevertheless, models were proposed, giving an idea on the structure of this type of compound. A first model was imagined by Piccolo and Stevenson in 1982 [13]. Then, a second model was developed by Schulten and Schnitzer in 1993 [15]. This revealed that humic acids are complex macromolecules made up of aliphatic chains and several aromatic cycles which carry carboxylic and salicylic functional groups (Fig. 1). Gardea-Torresdey and co-workers [14,24,25] showed that the humic acid carboxylic groups are essentially responsible for the fixation phenomenon. Before studying the interaction HA–metals, we chose to study model molecules–metal interactions. These models are structurally close to humic acid and will allow a validation of the study. Benzoic acid and catechol, having the carboxylic acid functional group (—COOH) or the phenol functional group (—OH) grafted on aromatic cycles were selected like model molecules. Our study on HA–metal interactions was carried out with a humic acid marketed by FLUKA TM Company (FHA TM) and another coming from the International Humic Substances Society (IHSS TM). The study of the interactions humic acid–metal was carried out by Fourier transform infra-red spectroscopy (FTIR). It allowed us to follow the variations of vibration frequencies of carboxylic functional groups observed in the average FTIR [14,26,27]. As in the study with lead, the vibration bands of carboxylic (—COOH) functional groups can undergo displacements and/or reductions in the intensities of absorption bands according to the nature and the concentration of the studied metal.

The main aim of this work is to understand: (i) the interactions of mercury with the carboxylic function, (ii) under which form (acid or salt) humic acid reacts efficiently with mercury and (iii) the affinity of humic acid towards mercury (mercury potential in sites occupation).

This study was supported by the analysis of metals by ICP-AES before and after each cation exchange.

2. Material and methods

2.1. Model molecules

Our study on the interaction model molecules–metal was carried out on the catechol C_6H_4—$(OH)_2$, the benzoic acid C_6H_5—COOH and the salicylic acid HO—C_6H_4—COOH with Hg^{2+}. The benzoic acid, the catechol and the salicylic acid were provided by Merck Company TM. The mercury acetate comes from Fluka TM Company. First it was proceeded by a sodium exchange by adding a NaOH solution (2M). Then the sodium catecholate and benzoate obtained underwent an exchange Na^+/Hg^{2+}. The experimental protocol is detailed in Fig. 2. It is noteworthy that under the addition of the 1st drop of mercury acetate or lead nitrate, catecholate, benzoate