

Interaction of humic substances and hematite: FTIR study

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Abstract: The present work extended the knowledge on the binding and complexation of humic substances (humic acid or fulvic acid) and hematite by Fourier transform infrared spectroscopy (FTIR). The FTIR data gained gave the consistent evidences by two different sampling preparation methods that the interaction mechanism between humic substances and hematite was mainly conform to the ligand-exchange involving carboxylic functional groups of humic substances and the surface sites of hematite. The present method, although associated with some uncertainties, provided an opportunity to increase the knowledge in this field.

Keywords: humic substances; fulvic acid; humic acid; hematite; FTIR; complex

Introduction

Interactions of humic substances (HSs) and iron oxides are of great significance in many geochemical processes. It is clear that adsorption of HSs to the surface of iron oxides can greatly influence the properties of such surfaces, thus potentially affect the fate, behavior, transport and transformation of environmental pollutants (Mcknight, 1992). On one hand, when adsorbed to surfaces of iron oxides, HSs may bind and hence immobilize trace metals, radionuclides, and nonionic organic pollutants, and they also alter oxide surface charge properties and flocculation kinetics (Marshall, 1998). On the other hand, HSs are also involved in the natural reduction of Fe(III). The dissolution of ferric oxides sensitized by surface Fe(III)-humate complex, has been postulated to be an important mechanism in controlling iron concentration in natural environments (Walte, 1994).

Most of iron oxides in the aqueous environment coexist with HSs, more importantly perhaps, HSs have encountered the iron oxides, thus coating the surface of iron oxides, prior to an influx of contaminants in many instances. Therefore, an understanding of the adsorption mechanisms, the structure of the adsorbed layers, and the influence of solution chemistry on the adsorption of HSs has significant environmental applications. However, a clear insight into interaction between iron oxides and HSs and further mechanistic elucidation in this binary solute system is far from being attained, due to the inherent intractability of HSs of which are considered to be complex macromolecular and ill-defined nature (Wang, 1997). Some hypotheses and mathematical models have remained elusive and are still causing speculations on account of scanty direct proofs. Such information is readily accessible through the profound analysis of reactive systems at the microscopic level accompanied by modern spectroscopic techniques. However, to date, only a few of spectroscopy studies are available to inspect interaction of HSs and iron oxides (Gu, 1994; 1996).

Many spectroscopic methods have been employed to

investigate HSs compositions and structures (Francioso, 1998). FTIR has proven to be one of the most powerful tools (Gu, 1994). FTIR spectroscopy of organic compounds may be used to furnish valuable information on the distinct chemical groups and/or related molecular structures present in the organic matter, including aliphatic chains, aromatic rings, organo-mineral complexes and functional groups occurring in individual components or in mixtures. These analyses contribute significantly to the molecular and conformational characterization of the humic substances. Likewise, a similar strategy should be fruitful to work over interaction between iron oxides and HSs in the current work.

The objectives of this research were to get insight into the binding mechanism between iron oxides and HSs by FTIR. The present study was conducted using a well-defined crystalline iron oxide phase (α -Fe₂O₃) and two HS samples.

1 Experimental section

1.1 Materials

Hematite was synthesized according to a previously published procedure (Matijevic, 1978). Particles of the iron oxide were deep red colored and appeared to be well crystallized with an average diameter of approximately 0.4–0.5 μm as viewed by TEM (Fig. 1). The X-ray diffraction pattern (Fig. 2) of the iron oxide matched exactly that of hematite and rounding of the baseline spectra indicated the presence of trace amounts of amorphous iron oxides. Sharp and symmetric peaks, indicating high crystallinity and large particle size characterized the expected compounds. The product is resuspended in a polypropylene bottle kept in the dark at 4°C. The same batch of hematite was used in all of the experiments. All solutions were prepared from analytical grade reagents and high purity water [“Q-H₂O”, resistivity $\geq 15 \text{ Mohm} \cdot \text{cm}^{-1}$]. The ferric nitrate solutions were passed through 0.22 μm Milipore filters to remove any particulate contaminants by means of a glass vacuum filtration unit (Sartorius, Göttingen, Germany) before being stored in Pyrex bottles.

The humic acid(HA) was gained as a gift, which was extracted from the fallen needle-leave soils. The sample sites were situated in Jilin Province, China. The fulvic acid(FA) was extracted from the Liaohe River situated in Liaoning Province in the northeast of China. The FA extraction procedure followed the protocol of the international humic substance society (IHSS), with some modifications (Chabbour, 2001). Both FA and HA solution was stored as a stock solution for further use.

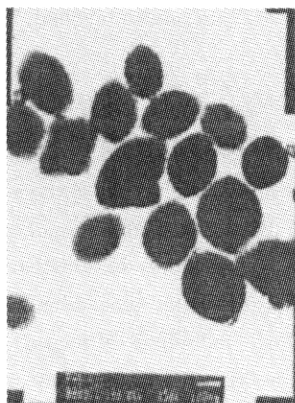


Fig.1 Electron micrograph of a soil obtained by aging a solution 0.018 mol/L in $\text{Fe}(\text{NO}_3)_3$ and 0.046 mol/L in HNO_3 for 24 h at 100°C

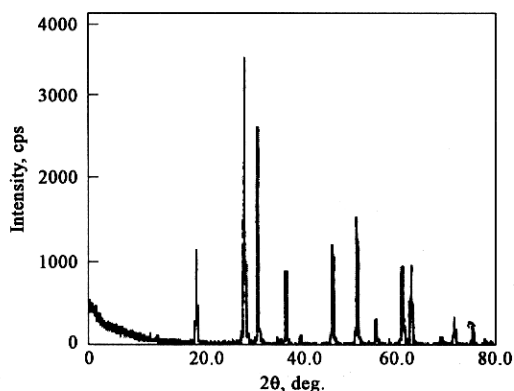


Fig.2 XRD pattern of the sample of hematite obtained by this experiment

1.2 FTIR study

The sampling preparation for FTIR was obtained by two different methods to gain more information. One group of samples for FTIR analysis were gained by mixing the FA or HA powder and hematite at 1 : 1 (w/w), diluted and conditioned to the desired pH, then stirring for 6 h, following that the solution was filtrated, washed to remove loosely bound FA or HA from the surface and dried at ambient temperature and powered. The other group of samples gained by mixture of the FA or HA powder and hematite at the same proportion under the desired pH, stirring for the same time, followed by directly dried at ambient temperature. All samples were stored in a desiccator until analyzed by the FTIR spectrometer. All experiments were performed at ambient temperature. The reaction environment was adjusted

by 0.1 mol/L HCl or 0.1 mol/L NaOH. A pH spectrometer (Sartorius, Göttingen, Germany) was used to measure pH in all samples. The electrode was externally calibrated using the standard solutions of known concentrations. The ionic strength was not controlled.

Solid-state Fourier-transform infrared spectra were recorded for a wavenumber range of 4000 to 400 cm^{-1} in a Nicolet, 20DXB(Nicolet Instrument Corp.) equipped with an IBM personal computer and Nicolet software. FTIR spectra were measured on KBr pellets prepared by pressing mixtures of 1 mg dry powered sample and 100 mg spectrometry-grade KBr under vacuum, with precaution taken to avoid moisture uptake. The major peaks(intensity and wavenumber) were found by using OMNIC software(Nicolet Instruments Crop.).

2 Results

Infrared spectroscopy has long been used for the structural studies of humic substances, particularly for defining the characterization of the surface interaction mechanism(Gu, 1994; 1996). These spectra were compared with one of the unloaded oxides sample to determine any changes observed, which included the emergence of new peaks, intensity variations of peaks originally present and wavelength shifts.

Fig.3 and Fig.4 show the FTIR spectra of solution FA before(A, B and C) and the corresponding spectra of FA interacted on hematite (A_1 , B_1 and C_1) at pH 2.8, 3.3, 4.5, 6.0, 7.1 and 8.2 after drying. The difference spectra were obtained by subtraction of the FTIR spectra of pure iron oxide from that of the iron oxide adsorbed with FA.

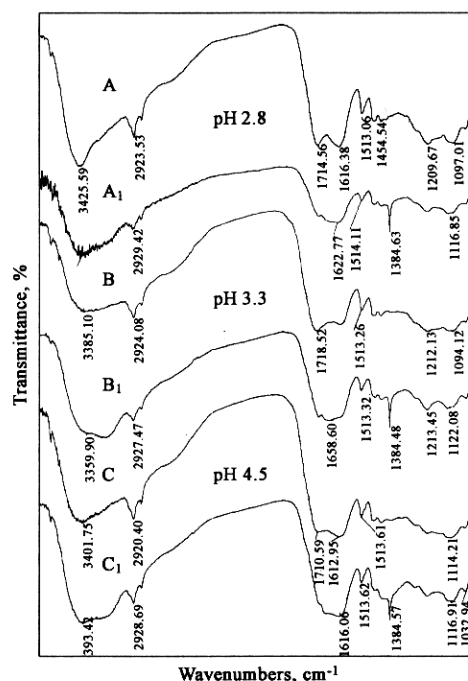


Fig.3 FTIR spectra of the FA before and after interplay with hematite at pH 2.8(A, A_1), pH 3.3(B, B_1) and pH 4.5(C, C_1)

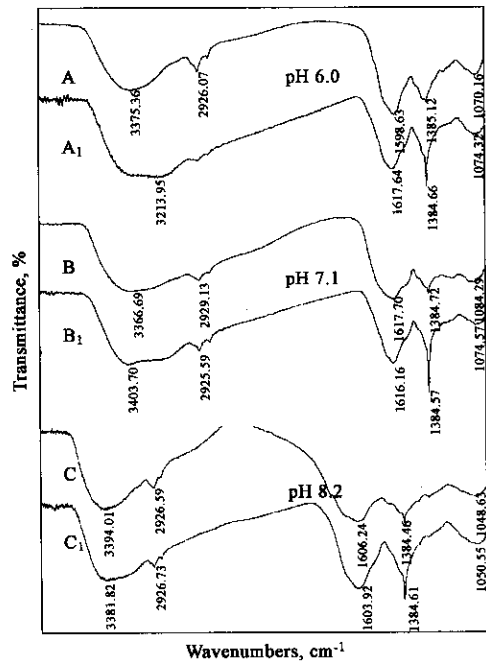


Fig.6 FTIR spectra of the HA before and after interplay with $\alpha\text{-Fe}_2\text{O}_3$ at pH 6.0(A, A₁), pH 7.1(B, B₁) and pH 8.2(C, C₁)

Spectrum (b) and (d) are the FTIR spectra of FA adsorbed onto the surfaces of hematite, which of the samples were prepared by interplay between FA and hematite, following filtration, washing and drying. There exhibited three major peaks at 476, 563, and 1621 cm^{-1} in spectrum (a). The peaks 1621 cm^{-1} may be due to hydrous components of the oxide, i.e., hydroxyl and water molecules, but the peak at 563 and 476 cm^{-1} may be attributable to the infrared active modes polarized perpendicular to the *c*-axis of the hexagonal crystal system(\parallel mode)(Wang, 1998). As compared with spectrum (b), there appears a new weak band in the region of 1402 cm^{-1} . Furthermore, the intensities of the band

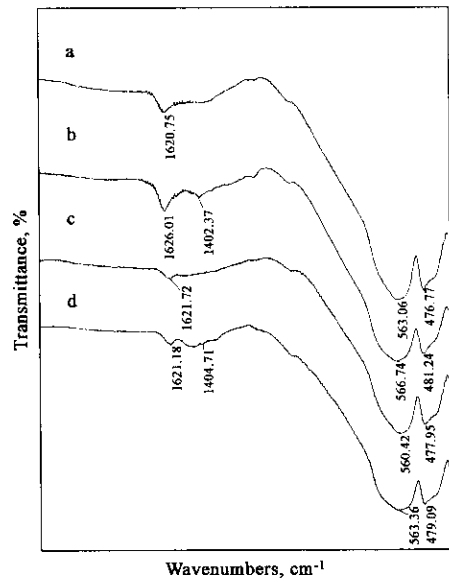
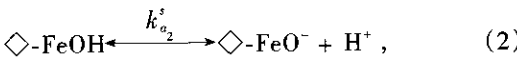
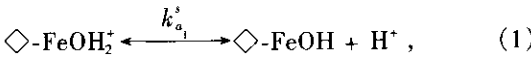


Fig.7 FTIR spectra of hematite before and after interplay with FA at pH 3 and 6

around 1600 cm^{-1} increased. The results display that FA adsorbed onto the surfaces of hematite and complexed with hematite by COOH or COO^- functional groups interplay with $\diamond\text{-FeOH}_2^+$ and $\diamond\text{-FeOH}$ of hematite surfaces. The amount of carboxylate groups are insignificant, there may be due to the loss of sampling preparation process.

3 Discussion

It has been well known that iron oxide surface species are noted as $\diamond\text{-FeOH}_2^+$; $\diamond\text{-FeOH}$; $\diamond\text{-FeO}^-$. The behavior of hematite is a function of the pH of solution due to the interaction of the oxide surface with H^+ . Surface modeling quantifies the electrostatic interactions between the oxide surface species and the ions at the oxide interfaces by way of the generalized two layers model. pH vs. surface species hematite is shown in Fig.8(Faust, 1989), which shows that $\diamond\text{-FeOH}_2^+$ fraction increases as the pH becomes more acidic, $\diamond\text{-FeOH}_2^+$ amounting to 50% at pH 6.0; 70% at pH 5.0 and 90% at pH 4.0. The fraction of the surface species $\diamond\text{-FeOH}$ is seen to negligible levels at $\text{pH} < 3.0$. The surface hydrolysis reactions for hematite can be written as (Eq. 1—4):



where

$$k_{a_1}^s = \frac{[\diamond\text{-FeOH}][\text{H}^+]}{[\diamond\text{-FeOH}_2^+]}, \quad (3)$$

$$k_{a_2}^s = \frac{[\diamond\text{-FeO}^-][\text{H}^+]}{[\diamond\text{-FeOH}]}. \quad (4)$$

As the model iron oxide, hematite adsorbed by HSs has been widely inspected in a laboratory scale(Gu, 1996). The results showed that a decrease in the adsorption of HSs with an increase of pH(Gu, 1994), which seems consistent with the anion exchange (or electrostatic interaction) mechanism

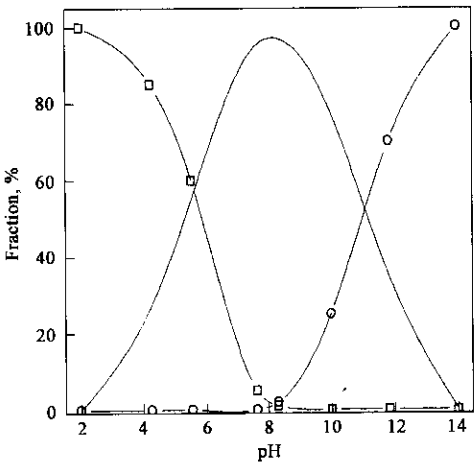


Fig.8 The distribution of surface species of hematite as function of pH
 FeO^- (○), FeOH (—), FeOH_2^+ (□)

because the surface of iron oxide becomes more positively charged as pH decreases. However, anion exchange is not considered to be the major mechanism in the system. Gu *et al.* (Gu, 1994) presented a range of evidence to suggest that ligand-exchange mechanisms whereby an organic ligand replaces H_2O or OH^- from the surface FeOH_2^+ and FeOH groups.

Ions can be bound by mineral surfaces by different mechanisms. Often a distinction is made between so-called inner sphere complexes (the ligand is coordinated to the metal atom of the surface) and outer sphere complexes (the ligands weakly interacts with the surface groups without formation of common ligands) (Filius, 1997). It is clear that the FA form inner sphere complexes with hematite surfaces via ligand exchange at the present study. At low pH, inner sphere complexes are important owing to their favorable charge distribution. With increasing pH, the carboxylic groups react predominantly via outer sphere complexes because the electrostatic interactions will increasingly favor outer over inner sphere complexation (Filius, 2002), which is corresponding to the results of FTIR.

The carboxyl functional groups of HSs are known to form very stable complexes with many metal cations or hydroxy metal cations (Leenheer, 1998). The complexation reactions are also supported by the studies with simple model organic compounds (Evanko, 1998). The modes of ligand exchange interactions between iron oxide and DOM may thus be postulated analogous to the binding of Fe^{3+} with DOM. Several possible modes of ligand exchange interactions between iron oxide and HSs may thus be postulated analogous to be binding of Fe^{3+} with fulvic acids. Possible structures for surface complexes are shown in Fig. 9. FTIR data showed that the peak around 1600 cm^{-1} , which is contribute to the asymmetric $\text{C}=\text{O}$ stretching in COO^- groups, varied slightly in frequency and intensity when the spectra of DOM disturbed by hematite at different pH. This may be understood as a result that there coexists different type of the

surfacial complexes. Thus, it is difficult to further speculate the structure information of the complexes by FTIR only.

4 Conclusions

Combined with the previous research, we had come to a general consensus that the complexation mechanism was governed by ligand-exchange involving carboxylic functional groups of HSs (including HA and FA) and the oxide surface sites. No other functional groups such as phenolic-OH participated in complexation. It should be stressed that FTIR spectroscopy was useful to furnish valuable information on the related molecular structures present in the complexation reaction occurred between HSs and iron oxides. By way of an appropriate data collection and interpretation of FTIR spectrum, characteristic peaks can be assigned and consequently, a complex mechanism occurred on the surface of iron oxides could be revealed.

The knowledge obtained here may contribute to the interpretation of the reactions involved these constituents occurred in nature. We also believe that further studies are needed to fully recognize the environmental significance of these results because of the complexity of natural systems.

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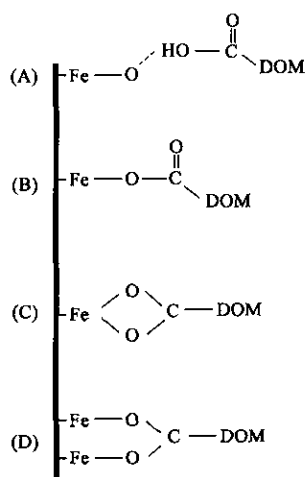


Fig. 9 Possible structures for surface complexes of organic acids sorbed hematite