

Depth profiling of soil clay-xanthan complexes using step-scan mid-infrared photoacoustic spectroscopy

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Abstract

Many soil micro-organisms produce extracellular polysaccharides (EPS); former studies demonstrate that EPS are produced in soil and are closely associated with the surrounding clay particles, and the formed clay-EPS complexes play an important role in soil biogeochemistry. In the present study, experimental clay-xanthan complexes were prepared as models for the soil/biota interface, and the step-scan function of FTIR-PAS technique was initially applied to *in situ* explore the characteristics of surface layers. The variances of depth profiling spectra of montmorillonite are higher than that of kaolin, and more xanthan information was observed in the depth profiling spectra of montmorillonite, which was specifically verified by absorption in the region of 600-1200 cm^{-1} . The xanthan structure changed significantly due to the interaction between xanthan functional group and clay surface. The surface of montmorillonite is more hydrophilic than that of kaolin as indicated by absorption at 1640 cm^{-1} ; montmorillonite seems to interact more easily with hydrophilic xanthan and a much broader surface layer was observed through depth profiling PAS spectra (9.8 μm vs 3.8 μm). The thicker surface layer resulted in stronger water retention capability, and may provide a basis for interpreting the variance of soil quality.

Key Words

Kaolin; Montmorillonite; Polysaccharides; Xanthan; Infrared photoacoustic spectroscopy

Introduction

Xanthan is a high molecular weight natural extracellular polysaccharides (EPS) produced by bacteria (Serenio *et al.* 2007), Many soil micro-organisms produce EPS, and former studies demonstrate that EPS are produced in soil and are closely associated with the surrounding clay particles as an amorphous sheath, and this sheath is in turn coated with clay minerals that are impregnated by EPS. The clay-EPS complexes play an important role in soil biogeochemistry (Chenu, 1993). Complexes of polysaccharides and mineral particles can be directly visualised using electron microscopy (Curry *et al.* 2007); the interaction mechanism of mineral particles is explained by the adsorption of EPS onto the mineral surfaces, creating attachment points and, by the formation of bridges, connecting different mineral particles altogether (Koegel-Knabner *et al.* 2008). NMR measurements (Simpson *et al.* 2006), and FTIR allow the understanding of the general mechanisms that govern the interaction of organic moieties with mineral particles. In spite of this accumulation of knowledge on these complexes (Huang *et al.* 2005), understanding at the spatial characteristics of interface layer occurring in these clay-polysaccharides complexes remains unclear due to the limit of *in situ* monitoring techniques.

Fourier transform infrared spectroscopy (FTIR) is a widely used analytical technique that is routinely applied for the characterization of soils (McCarty and Reeves, 2006) however, conventional infrared spectroscopic techniques, such as transmittance spectroscopy and reflectance spectroscopy, are usually used for homogeneous materials, and need sample pretreatments; thus, real time monitoring, especially for heterogeneous samples, can not be achieved using the conventional infrared techniques. Recently, a novel infrared technique, i. e. Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS), has been used in the soil analysis, and a good performance was obtained (Du *et al.* 2008). A photoacoustic (PAS) signal is generated when infrared radiation absorbed by samples is converted into heat within the sample. This heat diffuses to the sample's surface and into the adjacent atmosphere (usually, helium). Thermal expansion of this gas produces the PAS signal (Figure.2) (Irudayaraj and Yang, 2002). The signal generation process isolates a layer extending beneath the sample's surface, which has a unique function of *in situ* depth profiling, and this function will be useful in the study of heterogeneous or layered materials. Several depth profile studies of biological substances have been reported (Irudayaraj and Yang, 2002); however, to our knowledge, there is no study applying FTIR-PAS to depth profiling of soil organo-mineral complexes. The objective of the present study was to explore the characteristics of interface in soil organo-mineral complexes using the novel technique of FTIR-PAS; it is quite possible to roughly estimate the probing depth and to investigate the interface of organo-mineral complexes in the depth direction through FTIR-PAS measurements.

Methods

Soil clay

Source clays kaolin (KGa-1b) and montmorillonite (STx-1b) were used without purification (American Mineral Clay Society), the properties of the source clays were published in Patricia (2001). Xanthan was from *Xanthomonas campestris* (Sigma Chemicals).

Preparation of soil clay-xanthan complexes

Clay-xanthan complexes were prepared by mixing 2 g kg⁻¹ aqueous solution of xanthan with 100 g kg⁻¹ clay suspensions. The clay-xanthan mixtures were incubated in 25°C for 24 h, and centrifuged at 10000 g, then removed the supernatant; the residues were washed with deionized water twice, and then air dried in room temperature for use.

Recording of mid-infrared photoacoustic spectra

The photoacoustic spectra were recorded for all samples (clay, xanthan and clay-xanthan complexes) using a Nicolet 380 spectrophotometer (Thomalelemental, USA) equipped with a photoacoustic cell (Model 300, MTEC, USA). Briefly, the samples (about 200 mg) were placed in the cell holding cup (diameter 5 mm, height 3 mm), after which the cell was purged with dry helium (10 mL min⁻¹) for 30 s to minimize the interference due to water vapor and impurities. The samples were then scanned at wavelengths of 600–4000 cm⁻¹ with a resolution of 4 cm⁻¹ and a mirror velocity of 0.16 cm s⁻¹, 0.32 cm s⁻¹, 0.64 cm s⁻¹, and 1.89 cm s⁻¹. The PAS spectra were ratioed against a carbon black background, and 32 successive scans were recorded and the average value was reported.

Spectral data treatments

Photoacoustic spectra were pre-processed using a smoothing filter (Savitzky & Golay, 1964). Min-Max normalization was used during preprocessing of the filtered spectral data; Matlab 7.0 was used to do the above data analysis.

Results

Figure 1 depicts the FTIR-PAS spectra of kaolin measured at the various moving-mirror velocities. The spectral outline and band positions show no significant change with moving mirror velocities except the band densities. However, the intensities of bands at lower wavenumbers significantly increase relative to those at higher wavenumbers. A likely explanation for this tendency is saturation of the photoacoustic signal caused by an increase in the probing depth, which equates to an increase of sample thickness. Although the results described here provide no conclusive evidence to account for these changes of relative intensity with moving-mirror velocity, such changes can be, if the photoacoustic saturation occurs, regarded as proof that the FTIR-PAS spectra include a depth profile on the region closest to the surface of kaolin-xanthan complex.

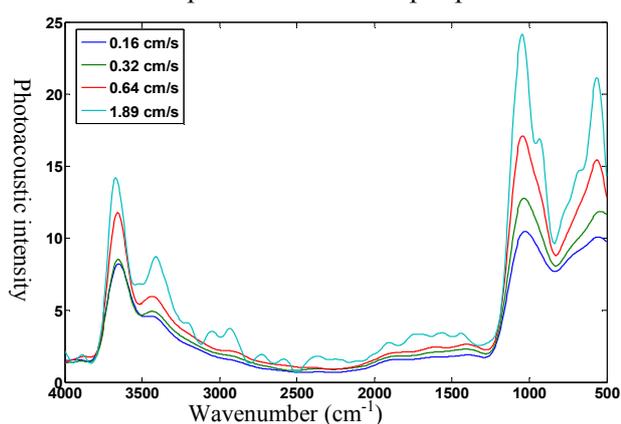


Figure 1. Depth profiling FTIR-PAS spectra of kaolin-xanthan complex

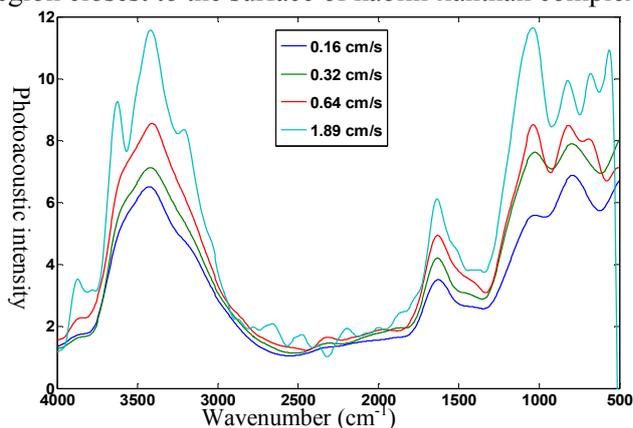


Figure 2. Depth profiling FTIR-PAS spectra of montmorillonite-xanthan complex

FTIR-PAS spectra of montmorillonite-xanthan complex under different moving mirror velocities are demonstrated in Figure 2. The band intensities significantly increase with increasing moving mirror velocity and the relative band intensities have significantly changed in the region of 600–1200 cm⁻¹. In other words, the intensities of the bands assigned to Si-O, Al-O decrease as the thermal sensing length becomes shorter. The spectral changes around 1640 cm⁻¹ indicate that the moisture content (both absorbed in montmorillonite

surface and combined with xantahn) increases. Xanthan is likely to significantly contribute to the water retention capability of montmorillonite-xanthan complex, but the contrition is less for kaolin-xanthan complex.

The photoacoustic probing depth should be determined from the shorter of the thermal diffusive length (μ_s) and the optical wave decay length (μ_β). The thermal diffusive length can be controlled by the moving-mirror velocity, because μ_s is given by

$$\mu_s = \sqrt{\frac{D}{\pi V \nu}}$$

for an opaque sample such as soil clay, where D is the thermal diffusivity of sample, V the moving-mirror velocity, and ν is the frequency of infrared radiation. Therefore, depth profiling is possible for the soil clay-polysaccharide complexes provided that μ_s is shorter than μ_β . μ_s of complex samples were roughly calculated with the typical thermal diffusivity of soil clay ($1.0 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$) under different moving mirror velocities and radiation frequencies (Table 1).

Table 1. thermal diffusion distance of soil clay-xanthan complexes calculated from the typical thermal diffusivity of soil clay ($1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$) against the specific infrared frequencies in wavenumber at various moving-mirror velocities

Mirror velocity, (cm s^{-1})	V	Thermal diffusion distance, μ_s (μm)		
		1040 cm^{-1}	1640 cm^{-1}	3400 cm^{-1}
0.15		14.3	11.4	7.9
0.32		9.8	7.8	5.4
0.64		6.9	5.5	3.8
1.89		4	3.2	2.2

The band of kaolin-xanthan complex spectra at 3400 cm^{-1} is influenced xanthan in the mineral surface (Figure 1). The change of band intensity is very small with the first two moving mirror velocities (0.16 cm s^{-1} and 0.32 cm s^{-1}). Hence, most of the probing depth is in mineral section. The intensity increases significantly with the moving mirror velocity of 0.64 cm s^{-1} , which means that the organic layer in the kaolin-xanthan complex accounts for some of the probing depth (3.8 μm). The intensity is stronger with mirror velocity of 1.89 cm s^{-1} , and the organic layer may contribute to most of the probing depth (2.2 μm). The kaolin surface layer can be roughly divided in to two layers: interface layer and xanthan layer, and the thicknesses are roughly evaluated as 1.6 μm and 2.2 μm , respectively. Water content is higher in the interface layer, while it is less in xanthan layer.

The main band changes are observed in the region of 600-1200 cm^{-1} in the depth profiling spectra of the montmorillonite-xanthan complex (Figure 2). The bands in this region with moving mirror velocity of 0.32 cm s^{-1} is significantly different from that with moving mirror velocity of 0.16 cm s^{-1} , but is similar with band under moving mirror velocity of 0.64 cm s^{-1} . Therefore, probing depth under moving mirror velocity of 0.32 cm s^{-1} can be regarded as montmorillonite surface layer, and probing depth under moving mirror velocity of 0.64 cm s^{-1} is likely as xanthan layer since the similarity with the absorption band under moving mirror velocity of 1.89 cm s^{-1} . Thus the montmorillonite surface layer can also be roughly divided in to two layers, and the thicknesses are roughly evaluated as 2.9 μm and 6.9 μm , respectively. Obviously, the thickness of the surface layer is much higher than that in kaolin surface. The great difference in surface layer may deprive from mineral surface properties as well as the xanthan conformations (helix or random coil) (Horton *et al.* 1985).

The thickness of the mineral surface layer will directly impact on soil quality, such as nutrient bioavailability, water retention, micro-organism diversity etc. Thicker surface layer has higher water retention capability, and more nutrients can be absorbed, which can be indicated by the fact that montmorillonite based soils are usually fertile than kaolin based soils. In real soil situations, organo-mineral complexes are complicated but clay-xanthan complexes can be the precursor of the complicated organo-mineral complexes (Lii *et al.* 2002), and a thicker surface layer may approximate real complicated organo-mineral complexes (Wattel-koekkoek *et al.* 2001). This initial study is based on relatively simple model clay-polysaccharide complexes, and it may provide some basic knowledge on the spatial configuration of real surface layers, however, the results need more exploration using various methods and involving more minerals and polysaccharides.

Conclusion

Soil clay and xanthan were successfully characterized using FTIR-PAS technique, and valuable information of the interface layer in the clay-xanthan complexes was obtained using the depth profiling analysis through FTIR-PAS. The profiling indicated that montmorillonite was more hydrophilic compared with kaolin, and thus more easily interacted with xanthan. The Montmorillonite-xanthan complex had a much thicker surface layer (both interface layer and xanthan layer), which resulted in a stronger water retention capability and favored the formation of more complicated soil organo-mineral complexes. The thicker surface layer may provide an inner mechanism for interpreting the variance of soil fertility.

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