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Determination of the adsorption process of tributyltin (TBT) and monobutyltin (MBT) onto kaolinite surface using Fourier transform infrared (FTIR) spectroscopy

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Abstract

In the present study, the interactions between kaolinite surfaces and adsorbed organotin molecules were investigated. The bonding mechanism and the effects to the crystal lattice were determined by means of Fourier transform infrared (FTIR) spectroscopy. Adsorption experiments were conducted at pH 4, 6 and 8. In order to examine the influence of the molecular structure on the adsorption process, two organotin compounds were used, namely tributyltin (TBT) and monobutyltin (MBT). Attraction of TBT to the kaolinite surface caused a strong decrease of OH bending modes as well as a decrease of the stretching vibrations of Al(Si)─O lattice groups at wavenumbers between 1400 and 800 cm^{-1}, while the OH stretching vibration modes at wavenumbers 4000 to 3000 cm^{-1} were not affected significantly. In contrast to this, the attraction of MBT molecules influenced the stretching modes at 3667 and 3651 cm^{-1}. These bonds are related to so-called “outer hydrogen” OH groups located at the surface and along broken edges of monocrystals. In addition, a pH-dependent increase of H─O─H vibrations at 1637 and 3470 cm^{-1} could be observed.

Depending on the molecular structure of the butyltin compounds, different surface complexes were found. According to our results, TBT occurring with trigonal–bipyramidal molecule structure are bonded by the formation of a mononuclear complex having monodentate configuration. In this case, one oxygen atom of a Al(Si)─O lattice group is directly bonded to the Sn atom of a TBT molecule. The adsorption of TBT molecules showing a tetrahedral configuration results from hydrogen bonding. MBT forms octahedral units in aqueous solution and the molecule is bonded to the kaolinite surface by reaction with the “outer hydrogen” groups of the clay minerals.

Keywords: FTIR spectroscopy; TBT; MBT; Adsorption; Kaolinite

1. Introduction

Butyltin compounds are used as stabilizing additives in different polymers as well as biocidic reagents in various pesticides and antifouling paintings. Due to its widespread industrial application, significant amounts of these pollutants have entered the environment. A survey of the industrial applications of butyltin compounds and the resulting ecotoxic risks are given in Hoch [1]. Tributyltin (TBT) exhibits a high toxicity to sensitive aquatic life, even at low concentrations of 1–2 ng/l. Though monobutyltin (MBT) is less toxic, it is also of environmental interest [2]. Therefore, a detailed knowledge about distribution and fate of these compounds in different ecosystems is of global pressing need. Previous studies have shown that the distribution of organotins in the aquatic system is strongly controlled by adsorption to sediment phase and suspended particles [3–6]. In general, sediments can be seen as an environmental sink for butyltin compounds [7] and clays play an important role as sorbent materials [8,9]. But adsorption is a reversible process and fixed butyltin molecules might be released from the sediment depending on environ-

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mental conditions, like pH and salinity [5,6,10]. With regard to this aspect, detailed information about adsorption mechanisms is helpful in order to estimate the ecologic risk and to develop reorganization measures for the decontamination of polluted systems.

In order to determine the interactions between solid surfaces and pollutant molecules, investigations of reactions at the particle/water interface are required. Spectroscopic measurements provide data which are helpful to explain surface complexation and bond formation. However, spectroscopic data for a TBT/mineral- and MBT/mineral-system at different pH levels are rarely. Hermosin et al. [11] studied the adsorption of MBT onto clay mineral surfaces and reported IR spectra of MBT/montmorillonite system at pH 2.5. Attachments of butyltin compounds towards silica surfaces described by IR spectroscopy were discussed in [12,13]. Eng et al. [14] determined the species of trialkylated organotins adsorbed to sediment phases by means of Mössbauer spectroscopy. The authors found out that tributyltin and triphenyltin are bonded to the sediment in form of hydrated cations. Unfortunately, no information about the pH of these experiments was given.

In general, interactions between organotin molecules and clay mineral surfaces can result in several surface complexes such as monodentate, bidentate, or bridging configurations. The stability of each configuration depends on numerous factors, like the structure of the surface and the formed complex, the coordination number of the metal atom in the complex or the electron configuration, the thermodynamic equilibrium constant of the reaction, pH of the medium, etc. The exact surface complex can only be obtained by direct spectroscopic measurements.

In order to give insights to the reaction at the solid/water interface a TBT/kaolinite and MBT/kaolinite system were investigated by means of Fourier transform infrared (FTIR) spectroscopy in the present paper. Kaolinite sample KGa was used in the adsorption experiments for several reasons: (a) kaolinite is an important component in natural sediments and (b) the physicochemical parameters and the surface properties of kaolinite sample KGa were well characterized in previous studies [15,16]. Such data are important to interpret and understand the adsorption process. Experiments were conducted with two organotin compounds (TBT and MBT) in order to discover an effect of the molecular structure on the adsorption mechanism. The results of the present study are seen as a contribution to explain the interaction between organotin molecules and mineral surfaces.

2. Materials and method

In the present study, the well-crystallized, low layer charged kaolinite sample KGa, obtained from the Clay Mineral Repositors, Columbia, USA, was used as sorbent material. Methanolic stock solutions containing each 2000 mg/l of tributyltin chloride (TBT >97% from Merck, Darmstadt, Germany) and monobutyltin trichloride (MBT >95% from Merck, Darmstadt, Germany), respectively, were prepared.

One gram of dried sample KGa was suspended into 50 ml of deionized water in a screw-capped Teflon flask. The pH value of the suspensions (pH 4, 6 and 8) was adjusted by addition of HCl or NaOH with an accuracy of ±0.1. Afterwards, the suspensions were spiked with appropriate aliquots of TBT or MBT stock solutions to yield a concentration of 5 μg Sn/ml in solution. The samples were shaken at $21 \pm 1\,^{\circ}\mathrm{C}$ for 24 h in the dark and than centrifuged at 2500 rpm for a period of 25 min. The supernatant liquid was poured off and the solid phase was dried at $35\,^{\circ}\mathrm{C}$ before analysing with FTIR spectroscopy. One kaolinite sample not contaminated with butyltin was prepared as described above for each pH.

2.1. Apparatus

Measurements were carried out by means of a JASCO FTIR 410 spectrometer. One centimetre diameter and constant-weight KBr pellets were prepared by mixing the sample KGa with KBr at 1:5 ratio. The spectra were measured in the wavenumber range of 400–4000 cm^{-1} with 256 scanning times at 4 cm^{-1} resolution. To interpret the spectra, the method of curve decomposition using curve fitting software was used. The parameters of the analysing technique were carefully adjusted to achieve the best fit and in all cases 99.9% of the spectra were reproduced.

3. Results

Kaolinite is characterized by a triclinic layer structure containing four OH groups in the primitive unit cell [17]. In order to interpret the effect of butyltin adsorption on kaolinite surface, the FTIR spectrum of an untreated kaolinite has to be explained in detail first (Fig. 1). The spectrum shows four characteristic stretching modes of the OH groups with wavenumbers around 3694, 3667, 3651, and 3619 cm^{-1}. According to Kristof et al. [18] these bands can be referred as follows: the band at 3694 cm^{-1} represents the stretching vibration modes of “inner surface hydroxyls” that are located at the surface of octahedral sheets opposite to the tetrahedral oxygens of the adjacent kaolinite layer. “Inner hydroxyls” are related to the stretching band centered on 3619 cm^{-1} and refer to OH groups located in the plane, common to octahedral and tetrahedral sheets as well as at a distance of 4.37 Å from the basal plane. “Outer hydroxyls” located at the surface and along broken edges of monocrystals are represented by stretching frequencies at 3667 and 3651 cm^{-1}.

The OH bending vibrations at 938 and 913 cm^{-1} can be referred to the “inner surface hydroxyls” and “inner hydroxyls” [19]. According to Marel and Beutelspacher [20], these bands are mainly caused by Al–OH groups. Bands centered at 1114 and 1102 cm^{-1} are referred to Si–O stretching vibrations, while the bands at 1032 and 1008 cm^{-1} are rather