



Pyrene photochemical species in commercial clays

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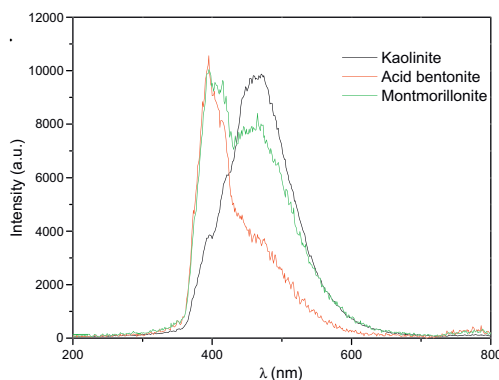
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HIGHLIGHTS

- ▶ Pyrene photochemistry on three commercial clays was investigated.
- ▶ Fluorescence monomers and excimers from pyrene were detected.
- ▶ Excimer formation is function of the amount Pyrene of adsorbed on the clay.
- ▶ Emission from pyrene crystals was detected for high loading samples.
- ▶ Lifetime distribution analysis identified all pyrene emissions and their lifetimes.

GRAPHICAL ABSTRACT



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ABSTRACT

The photochemistry of pyrene, a polycyclic aromatic hydrocarbon, adsorbed on kaolinite, sodium montmorillonite and acid bentonite K10[®] was investigated to determine how the concentration and structure of the clay minerals affect the formation of different species of pyrene. Fluorescence emission spectra were obtained using reflection geometry for pyrene at the concentrations ranging from 0.5 to 100.0 $\mu\text{mol g}^{-1}$ (pyrene:clay). Two pyrene photochemical species were observed, the monomer, which fluoresces at 396 nm, and its excimer which fluoresces at 470 nm. The formation of excimers occurred first on the kaolinite, due to the smaller surface area. In the acid montmorillonite, the fixed interlamellar space provided greater specific area, leading to lower formation of excimers. Emission from pyrene crystals was also detected for samples with high loadings.

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1. Introduction

Environmental problems caused by spillages, discharges or accidents involving fossil fuels and their derivatives are common.

It is of particular interest the determination of the compartment of these substances in the soil and their destination once reaching it (Azevedo et al., 2007). Among the fuel components, polycyclic aromatic hydrocarbons (PAHs) have received a great deal of attention due to their carcinogenic potential (ATSDR, 1995) and their significant environmental impact (Rolle et al., 2011).

The soil acts as a filter, as a function of its adsorption capacity, both retaining the nutrients required by plants and immobilizing

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pollutants, so reducing their movement and leaching towards sensitive areas (ex. water bodies) certainly contributes to diminishing their availability in the food chain (Chiou, 2002; Young and Weber, 2005; Macht et al., 2011; Bertagnolli et al., 2011).

Among the soil components responsible for this adsorption, the action of the organic component stands out, such that most studies correct for the level of organic matter present in the soil (K_{OC} or K_{OM}) when calculating the partition constant (K_D) (Schwarzenback et al., 2003; Grotenhuis and Rijnaarts, 2011). However, under certain circumstances, the clay fraction is observed to participate significantly as the sorption power of the soil increases, notably when there is a low level of organic matter in the soil (Hwang et al., 2003; Zhu et al., 2004; Maliszewska-Kordybach, 2005). Important differences between soils from the tropical and cold or temperate region must also be considered. Among the differences, the soil of the tropics are more acidic and have fewer weathered minerals because the 2:1 mineral transformation, such as of smectite and micas into kaolinites with low crystallinity (Schaefer et al., 2008).

Pyrene, a polycyclic aromatic hydrocarbon, is a very versatile fluorescent probe. Frampton et al. (2000) studied the structure of pyrene at low temperature and determined that the *c* plane (the height within the crystalline cell) of the pyrene molecule is 8.260 Å. Pyrene can form excimers. X-ray diffraction and Raman studies have shown that there are two possible conformations: face-to-face or stacking geometry, where the rings directly overlay each other and are sometimes shifted; and perpendicular geometry, where one molecule is perpendicular to the other. The pyrene excimer molecules are separated by 3.44–3.56 Å and the axis may be dislocated by 0.78 Å (Zallen et al., 1976; Jones et al., 1978).

The fluorescence emission spectrum of pyrene in hydrophobic solvents is characterized by the presence of monomers that have three very characteristic vibronic bands. These bands appear at 372, 384, 391 and 412 nm and correspond to the vibronic modes of the $S_1 \rightarrow S_0$ emission (Mohanambe and Vasudevan, 2006). In turn, studies to characterize the species of pyrene adsorbed on different solid surfaces have shown the existence of two photochemical species: the monomeric species, with maximum emission at 396 nm and its excimer (pyrene dimer in the excited state) at 470 nm (Bauer et al., 1983; Oliveira et al., 2004).

In a study of the emission of pyrene adsorbed onto synthetic expansive clay, laponite, Labbé and Reverdy (1988) observed that increasing the concentration of pyrene led to the formation of excimers. After lyophilization of the clay sample containing the pyrene excimer species, the authors observed that the intensity of the excimer decreased and that the emission of the vibronic bands for the monomer increased. However, this phenomenon was reversible. That is, adding water caused the clay to swell and the excimer species to regenerate. According to the authors, this fact is attributable to the presence of water in the interlamellar space, which increases the polarity of the medium, repelling the pyrene molecules and generating the excimer. A similar result was obtained by Cione et al. (1998) when studying the emission of naphthalene in synthetic expansive clays: a montmorillonite and a laponite. The authors observed that as the montmorillonite is an expansive clay with a greater degree of hydration reason why the emission intensity of the excimer was greater than that observed for the laponite.

The objective of this study is to elucidate the behavior of pyrene in clay minerals extracted from Brazilian deposits (kaolinite and montmorillonite), which are representative of the minerals found in tropical soils, and to compare them extracted with a commercial expansive acidic clay (bentonite K-10[®]).

2. Experimental

2.1. Materials

Commercial sodium montmorillonite and kaolinite clays were supplied by Bentonit, Brasil[®] and acid bentonite K10[®] was purchased from Aldrich. Pyrene was purchase from Aldrich, in the highest purity available (99%) and was used as received. All the solvents used for sample preparation were from also from Aldrich, Chromasolv Plus grade.

2.2. Characterization of clays

The surface specific area of the clay were determined adsorption-desorption of nitrogen at 77 K using Micromeritics A.S.A.P. 2000, using BET equation and the external surface area was determined by BJH equation.

2.3. Pre-treatments for X-ray diffraction identification of mineralogical composition of the commercial clays

The commercial clay samples (50 g) had the organic matter removed by sodium pyrophosphate and were then treated with dithionite–citrate–bicarbonate to extract the iron (Mehra and Jackson, 1960; Śrudoń, 2009). They were then dispersed by vigorously shaking (± 12000 rpm) in 250 cm³ of a 1 M L⁻¹ NaOH solution. After 15 min, the dispersion was sieved with a 0.053 mm mesh, dried at 40 °C and then analyzed by X-ray diffraction (Embrapa-Empresa Brasileira de Pesquisa Agropecuária, 1999; Jackson, 2005; Calderano et al., 2009).

2.4. Preparation of the oriented slides for X-ray diffraction

A 3 g sample of clay was placed in a centrifuge tube (model Supra 22 K, Hanil) with 40 cm³ of distilled water. The mixture was sonicated (model Sonifier 250, Branson) for 3 min to fully disperse the clays (Macht et al., 2011; Silva et al., 2012). After centrifuging at 18000 rpm, approximately 1 g of the sample was transferred to a glass microscope slide and wetted until it formed a homogeneous paste. Another glass slide was used to smear the sample to orientate the clay particles. Then the slide was dried at room temperature and analyzed by (total) X-ray diffraction. However, in order to allow the differentiation and identification of the clays, due to effects on the basic spacing, some treatments were performed: the solvation with ethylene glycol, heating treatments at various temperatures, and cation saturation with Ca, Mg and K to minimize the fluctuations of water between the layers of the crystal (Brindley and Brown, 1980). In that context, 1 g of the material was saturated with 1 M dm⁻³ CaCl₂ and another 1 g with 1 dm³ KCl. These were then washed with double distilled water to remove the excess ions and new oriented slides were prepared (Omotoso and Mikula, 2004; Senna et al., 2008). Diffractograms were obtained for clay samples: natural, dried at room temperature, (total); saturated with Mg to differentiate expansive 2:1 minerals (vermiculite and smectite) from the non-expansive (micas) mineral (Mg); saturated with Mg, followed by solvation with ethylene glycol to differentiate vermiculite from smectite (Mg Glycol); saturated with K to differentiate chlorite and vermiculite (VHE) and smectite (EHE) with Al-hydroxyl interlayered with expansive 2:1 minerals (K) and saturated with K and heated to 110, 350 and 550 °C to differentiate chlorite from VHE and EHE (K 110, 350 and 550 °C) (Bortoluzzi et al., 2008; Melo et al., 2009). The minerals were identified from the peaks corresponding to the $\langle 001 \rangle$ plane, following Brindley and Brown (1980). X-ray diffractograms were obtained using a Rigaku diffractometer, model mini-

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