



Research paper

Adsorption of picloram herbicide on iron oxide pillared montmorillonite

Jose L. Marco-Brown^a, C. Martín Barbosa-Lema^a, Rosa M. Torres Sánchez^b,
Roberto C. Mercader^c, María dos Santos Afonso^{a,*}

^a Departamento de Química Inorgánica, Analítica y Química Física e INQUIMAE, FCEN, UBA, Ciudad Universitaria, Pabellón II, C1428EHA, Buenos Aires, Argentina

^b CETMIC (Centro de Tecnología en Minerale y Cerámica), Camino Centenario y 506, CC (49) (B1897ZCA) M. B. Gonnnet, Argentina

^c Departamento de Física, IFLP, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina

ARTICLE INFO

Article history:

Received 10 August 2010

Received in revised form 20 December 2011

Accepted 3 January 2012

Available online 8 February 2012

Keywords:

Montmorillonite

Picloram

Pillared clay

Herbicides

ABSTRACT

The adsorption of picloram on Fe Oxide Pillared Clays (PILC) as a possible basis for the development of adsorbent materials for the remediation of polluted environments was studied. To this end, after characterizing PILC obtained from raw clay from Wyoming, USA by XRD, elemental analysis, Mössbauer spectroscopy, DTA, TGA and N₂ adsorption (BET), the picloram adsorption was studied at constant pH and ionic strength after 48 h equilibration with an aqueous solution of PCM. PCM adsorbed samples were characterized by SEM, zeta-potential vs pH functions, FTIR and TGA-DTA and the adsorption was modelled using Langmuir and Freundlich models.

The results reveal that the surface area and interlayer space of PILC are bigger than those of raw montmorillonite. An analysis of the adsorption isotherms of picloram on the PILC showed that picloram adsorption increases with decreasing pH. The adsorption of PCM on PILC was 150 times higher than that found for raw montmorillonite under similar conditions. The zeta-potential vs pH functions shape and FTIR indicated that PCM coordinates the surface iron centers throughout pyridinic nitrogen atom forming inner-sphere complexes. The much greater PCM adsorption on PILC turns the process into an excellent candidate to be used for dosing or remediation of pesticides.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Pesticides are widely used for control of broad-leaf weeds and other vegetation. The behavior of pesticides in soil is a large dynamic phenomenon. After application, they may pass into streams, rivers (Palma et al., 2004) and lakes or leach through soil with the possibility of contaminating subsurface waters (Zhang et al., 2000). Soils can be considered, to a first approximation, as a combination of the minerals that compose them (Taubaso et al., 2004). Since clays are one of these components with higher chemical reactivity, the study of the pesticides adsorption may be used as models for the overall behavior. Among the clays used to understand the adsorption behavior of several herbicides, montmorillonite clay mineral stands out among them because of their, low cost, high specific surface area, (Bojemueller et al., 2001) and evidence of the intercalation of the pesticides in the clay mineral interlayer can be followed by modifications of the (001) reflection (Aydin et al., 2009; Bojemueller et al., 2001; Chen et al., 2009; Cornejo et al., 2008; Damonte et al., 2007; Hocine et al., 2004; Khoury et al., 2010; Lombardi, et al., 2006; Suciú and Capri, 2009; Torres Sánchez et al., 2011; among others.).

Picloram, 4-amino-3,5,6-trichloropyridine-2-carboxylic acid (PCM) is a systematic herbicide that is used to control unwanted woody plants, broadleaf and deeply rooted herbaceous weeds in cereals such as wheat, barley, sugarcane and oats (FAO, 2007; Palma, et al., 2004; Zhang, et al., 2000). PCM is the most persistent herbicide of the chlorobenzoic acid family. One year after its application 10–30% of the amount of the applied herbicide was detected in some crops in Canada (Meru et al., 1990).

The anionic character of PCM at the pH of most soils and water environments (pK_a ≈ 2.3) generates its very low adsorption on soil particles and extremely high soil mobility (Biggar et al., 1978; Celis et al., 2002; Cheung and Biggar, 1974; Osteryoung and Whittaker, 1980). However, in soils with different contents of organic matter and clay minerals a relation between PCM adsorption and organic matter content was found (Biggar et al., 1978; Farmer and Aochi, 1974; Grover, 1971; Hamaker et al., 1966). Adsorption of PCM by clay minerals had been observed in very acid systems (Biggar et al., 1978), but no adsorption had been determined at pH values higher than 3 (Celis et al., 2002; Grover, 1971). Nevertheless, adsorption studies of picloram on non-modified clay minerals have indicated a low adsorption up to pH 9 (Marco-Brown et al., 2008).

Among clay substances, pillared clays (PILC) are interesting materials to be used as catalysts and adsorbents, due to its multi-charged centers, large area, high interlayer space and thermal stability. PILC synthesized with oxide pillars of Cr, Zr, Al, Ti, and Fe have been previously

* Corresponding author. Fax: +54 11 4576 3343.

E-mail address: dosantos@qi.fcen.uba.ar (M. dos Santos Afonso).

used in studies of adsorption of organic compounds (Cheknane et al., 2010; Tchieda et al., 2010; Zermane et al., 2010; Zuo et al., 2011; among others) as well as toxic metals such as As, Cd, Cr, Co, and Cu (Belkhadem et al., 2008; Bhattacharyya and Gupta, 2008; Cañizares et al., 1999; Heylen and Vansant, 1997).

This work aims at studying the PCM adsorption on iron oxide pillared montmorillonite, which could serve to develop adsorbent materials for the remediation of polluted environments and to design materials for controlled release of herbicides.

2. Materials and methods

2.1. Materials

PCM (inset in Fig. 1) was supplied by Sigma-Aldrich Co., purity 100%, solubility in water 430 ppm, $pK_a = 2.3$ (Pavlovic et al., 2005) and used as received. All other chemical reagents were provided by Merck PA and used without any further purification. Water was purified in a Milli-Q system from Millipore Inc.

Montmorillonite API # 26, Clay Mineral Spur Wyoming was provided by Ward's Natural Science Establishment, Inc., USA. This montmorillonite (labeled Mt) was manually milled in an agate mortar and sieved to a particle size of less than 125 μm . The main properties determined in a previous work (Marco-Brown et al., 2008) are: purity >98%, cation exchange capacity (CEC) 128 meq/100 g, isoelectric point ($\text{IEP}_{\text{pH}} = 3.2$), external surface area 27 m^2/g and total specific surface area 611 m^2/g (Michot and Villieras, 2006). The structural formula and isomorphous substitutions of Mt were determined from the chemical analysis following the method of Siguin et al. (1994).

2.2. Preparation of pillared clay

The pillaring solution with 1 M concentration of Fe(III) was prepared by dissolution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ salt at room temperature with the slow addition and vigorous stirring of a 2 M solution of KOH, until reaching a ratio of $\text{OH}^-/\text{Fe} = 2$. The pH was controlled to attain a value lower than 1.8 by adding drops of 6 M HCl when necessary. Afterward, the solution was kept at room temperature for 4 h with continuous stirring for aging.

Furthermore, a deionized water dispersion of 1 wt.% of Mt was mixed with the pillaring solution with a Fe/Mt ratio of 60 mmol Fe/g Mt. The mixture was allowed to react, stirring at room temperature for 12 h. Later on, the solid was obtained by centrifugation and washed by successive re-dispersions in deionized water followed by centrifugation until conductivity value lower than 10 μS was attained. Further the product was air-dried, heated at 300 $^\circ\text{C}$ for 2 h and denoted as Fe-PMt.

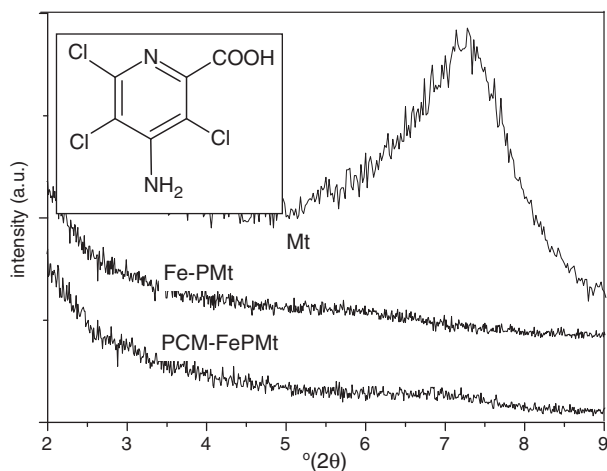


Fig. 1. XRD diffraction patterns of Mt, Fe-PMt and PCM-Mt.

2.3. Material characterizations

Composition of the Mt and Fe-PMt samples was determined by chemical analysis.

The specific surface area was determined by water adsorption at room temperature (S_w) (Torres Sánchez and Falasca, 1997) and nitrogen adsorption at 77 K (S_{N_2}) on samples previously dried at 100 $^\circ\text{C}$ for 6 h at high vacuum using a Micromeritics AccuSorb 2100 E equipment internal or interlayer surface (S_i) was determined as the difference between total and external surfaces, S_w and S_{N_2} respectively.

The X-ray diffraction patterns (reflection (001), counting time of 10 s/step collected from 3 to 13 $^\circ$ (2θ)) were obtained using a Philips 3020 with Cu $K\alpha$, 30 mA and 40 kV. Samples were X-rayed as semi-oriented at constant humidity (dispersion samples were dried maintaining a constant relative humidity (rh) of 0.47 for 48 h).

The electrophoretic mobility was determined in dispersions of Mt, Fe-PMt and Fe-PMt loaded with different amounts of PCM (PCM-FePMt) by microelectrophoresis in a Brookhaven equipment, using 10^{-3} M KCl as inert electrolyte. Samples were prepared at several pH values, and the content of total adsorbed PCM was measured.

The thermogravimetric measurements (TGA) were performed on 35 mg sample in a Shimadzu instrument (TGA-51H respectively), from room temperature to 800 $^\circ\text{C}$ at heating rate of 10 $^\circ\text{C}/\text{min}$, in nitrogen atmosphere.

Scanning electron microscopy (SEM) was performed using a file emission gun scanning electron microscope Zeiss (FEG-SEM Zeiss LEO 982 GEMINI) with combined Energy Dispersive X-ray Analyzer (EDS), which provides the qualitative and semiquantitative composition of the samples. The SEM images were taken by applying 5 kV voltage with different magnification times for the clarification of surface. Mt, Fe-PMt and PCM-FePMt were fixed to 10 mm metal mounts using carbon tape and spit coated with gold under vacuum in an argon atmosphere. The surface morphology of the coated samples visualized by SEM permitted the identification of interesting structural features on the sample surfaces. INCA software was used to determine the elemental composition of the surface before and after solute binding.

Mössbauer spectra were taken in a conventional constant acceleration spectrometer of 512 channels with a 50 mCi nominal activity $^{57}\text{CoRh}$ source in transmission geometry. The absorbers were powder samples of about 105 mg cm^{-2} for both samples, calculated after the method described by Long et al. (1983), that yields the optimum absorber thickness. Isomer shifts were calibrated against an $\alpha\text{-Fe}$ foil at room temperature. Mössbauer spectra were analyzed with version 1.05 of the Recoil program (Lagarec and Rancourt, 1998).

Fourier-Transform Infrared Spectra (FTIR) of Fe-PMt, PCM and PCM-FePMt samples were recorded on FTIR Nicolet 8700 spectrometer using KBr discs in the 500–4000 cm^{-1} region. The PCM-FePMt sample was prepared at pH 5 by four successive adsorption processing using 10^{-3} M KCl solution as inert electrolyte, this accumulative adsorption process allowed to reach a surface coverage of $\Gamma = 580 \mu\text{mol/g}$.

2.4. Adsorption experiments

The clay mineral dispersion in deionized water (16 g clay/L) was previously adjusted at a determined value of pH of 3, 5 or 7 adding drops of concentrated HCl or KOH solution. After that, a determined PCM concentration, $C_{0,\text{PCM}}$, was added to the clay mineral dispersion. All dispersions were prepared in 10^{-3} M KCl solutions, at temperature of $T = 25 \text{ }^\circ\text{C}$, with variable pH ranging between 3 and 7. The dispersion pHs were kept constant during the whole experiment.

The range of $C_{0,\text{PCM}}$ used in the adsorption isotherms was from 41 to 4970 for pH values of 5–7 and from 41 to 1657 μM for pH 3, respectively. The $C_{0,\text{PCM}}$ maximum concentration was established by the low solubility of PCM.

Download English Version:

<https://daneshyari.com/en/article/1695298>

Download Persian Version:

<https://daneshyari.com/article/1695298>

[Daneshyari.com](https://daneshyari.com)