New insights on the structure of the picloram–montmorillonite surface complexes

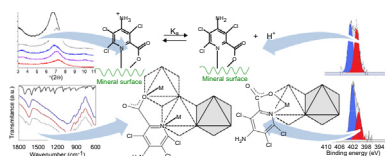Jose L. Marco-Brown [a], María Alcira Trinelli [a], Eric M. Gaigneaux [b], Rosa M. Torres Sánchez [c], María dos Santos Afonso [a],*

[a] Departamento de Química Inorgánica, Analítica y Química Física e INQUIMAE, FCEN, UBA, Ciudad Universitaria, Pabellón II, C1428EHA Buenos Aires, Argentina
[b] Université Catholique de Louvain, Institute of Condensed Matter and Nanosciences (IMCN), Division Solids, Molecules and Reactivity (MOST), Croix du Sud 2/L7.05.17, B-1348 Louvain-la-Neuve, Belgium
[c] CETMIC (Centro de Tecnología en Minerales y Cerámica), Camino Centenario y 506 CC (49) (B1897ZCA) M. B. Gonnet, Argentina

GRAPHICAL ABSTRACT

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ABSTRACT

Hypothesis: The environmental mobility and bioavailability of Picloram (PCM) are determined by the amine and carboxylate chemical groups interaction with the soils mineral phases. Clay particles, such as montmorillonite (Mt), and the pH value of the media could play an important role in adsorption processes. Thus, the study of the role of soil components other than organic matter deserves further investigation for a more accurate assessment of the risk of groundwater contamination.
Experiments: Samples with PCM adsorbed on Mt dispersions were prepared at pH 3–9. Subsequently, the dispersions were separated, washed, centrifuged and stored at room temperature. Picloram (PCM) herbicide interaction with surface groups of montmorillonite (Mt) was studied using XRD, DTA, FTIR and XPS techniques.
Findings: The entrance of PCM into the Mt basal space, in two different arrangements, perpendicular and planar, is proposed and the final arrangement depends on PCM concentration. The interaction of PCM with Mt surface sites through the nitrogen of the pyridine ring and carboxylic group of PCM, forming bidentate and bridge inner-sphere complexes was confirmed by FTIR and XPS analysis. The acidity constant of the PCM adsorbed on the Mt surface was calculated.

1. Introduction

The behavior of pesticides in the environment is a dynamic phenomenon. After application, they can reach streams, rivers [1] and lakes, or leach through soil with the possibility to contaminate subsurface waters [2,3]. Hence, better knowledge of the processes controlling the behavior of pesticides in soils for the protection of aquifers and streams is needed [4]. The adsorption of pesticides

by soil components is a key process to determine the availability of toxic substances in the soil and their transport to surface and groundwater [5].

Picloram, 4-amino-3,5,6-trichloropyridine-2-carboxylic acid (PCM), is a synthetic organic chemical belonging to the pyridine family of herbicides and also classified as a chlorinated derivative of picolinic acid. Pesticide activity is reported as a systematic herbicide that regulates plant growth. It is used to control annual broadleaf weeds at low rates and deeply rooted herbaceous weeds, vines and woody plants at higher rates in cereals such as wheat, barley, sugarcane and oats [1,6,7]. PCM had been detected in fresh water in a concentration range between 0.3 µg/L [1] and 437 µg/L [8]. The maximum level of picloram contamination in drinking water, recommended by EPA (Environmental Protection Agency, USA), is 0.5 mg/L. Concern about the environment and human health generated the need to seek adsorbents to diminish the concentration of PCM in fresh water and understand the interactions involved.

PCM has an anionic character at the environmental pH of most soils and water ($pK_a \approx 2.3$), which induces very low sorption on soil particles, especially on mineral clays. As a consequence PCM has extremely high soil mobility and was classified as a pesticide with a high leaching potential [9–13]. Basic amine centers and carboxylate groups of the PCM molecule are the responsible groups for the molecule interaction with the adsorbent surface active sites.

The contribution of mineral phases to the availability of pesticides in soils is often considered unimportant and overlooked [14]. Organic matter (OM) has been recognized as the main soil adsorbent but, adsorption on OM cannot always completely explain the pesticide retention in soils. Indeed, chemical groups in the surface of clay particles and the pH value of the media could play an important role in adsorption processes [15]. Then, the study of the role of soil components other than organic matter deserves further investigation for a more accurate assessment of the risk of groundwater contamination.

Soils with different organic matter and clay mineral contents have thus been used to adsorb PCM and a direct relationship between PCM adsorption and organic matter content has been found [11,16,17]. Adsorption of PCM by clays has been reported in very acidic condition [11], while for pH values above 3, PCM adsorption has not been detected [9].

The high cationic exchange capacity and specific surface area of montmorillonite allowed it to be used as target clay mineral to evaluate the sorption of pesticides [18–20] or amino acids [21]. The cationic pesticides thiabendazole and benzimidazole have been proven to highly adsorb on montmorillonite [22,23], while adsorption of a zwitterion such as glyphosate has also been evaluated on montmorillonite and its thermally treated form [24,25].

In previous work [26] it was found that interactions of PCM with clay mineral surfaces showed an anionic profile, with the adsorption decreasing when pH increasing, suggesting that the adsorption of PCM anions was coupled with a release of H_2O or OH^- ions. Also, the increase of Γ_{ads} with C_{eq} after an adsorption plateau indicated the existence of successive adsorption processes over different active sites [26]. PCM adsorption on montmorillonite showed evidence of a first monolayer formed up to a certain value of C_{eq} similarly to what has been found for glyphosate and zearalenone [25,27], and above this concentration other sites participated in the adsorption process.

The aim of this work is to study the structure of the surface complexes of PCM adsorbed on montmorillonite through the use of different experimental methods to get a better understanding of the fate of PCM on soil that, finally, determine the mobility and bioavailability of the herbicide on the environment.

2. Experimental

2.1. Materials

Analytical picloram (PCM) (Fig. S1) was supplied by SIGMA (purity 100%, solubility in water 430 ppm (1.78×10^{-3} M), pK_a = 2.3. [28], Mr = 241.5 g mol^{-1}) 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 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 less than 125 µm. The main properties reported in a previous work [26] were: CEC 138 meq/100 g determined by the formaldehyde method [29], purity >98% determined by XRD [30] and isoelectric point at pH = 3.2 (diffusion potential method [31]).

The structural chemical formula including isomorphic substitutions of Mt ($[(Si_{3.94}Al_{0.06})(Al_{1.56}Fe_{0.18}Mg_{0.26})O_{10}(OH)_2]M_{0.32}^+$) were determined from the chemical analysis following the method of Siguin et al. [32].

2.2. Samples preparation

Adsorption of PCM on Mt dispersions was made as indicated in a previous work [26]. Samples were prepared at pH 3–9 using a PCM initial concentration ($C_{0,PCM}$) ranging from 1.7 to 5.0 mM at constant ionic strength of 1.0 mM KCl. The dispersions were shaken and equilibrated for 48 h at room temperature, adjusting pH (3, 5, 7 or 9) with drops of HCl or KOH solutions. The dispersion pH values were kept in ±0.1 units. The $C_{0,PCM}$ maximum concentration used was established by the low solubility of PCM (1.7 mM for pH 3 and 5.0 mM for pH 5, 7 and 9). Subsequently, the dispersions were centrifuged at 17,000 rpm and the pellet obtained was separated from the supernatant solution. The solids were washed with distiller water several times, centrifuged and stored in desiccators over silica gel, at room temperature, for further analysis and labeled, e.g., as PCM–Mt1.7 for a sample prepared from a PCM solution with $C_{0,PCM}$ = 1.7 mM. Control samples, without PCM, were prepared following the same procedure.

Additionally a mechanical sample of Mt and PCM (denoted as MMS) was obtained for comparing purposes by mixing 5.0 g of Mt with 0.036 g of PCM in a mortar.

2.3. Characterization of the adsorbent and adsorption products

Nitrogen adsorption–desorption isotherms were recorded at 77 K using a Micromeritics ASAP 2010 instrument. Sample Mt was degassed for 12 h at 150 °C prior to measurement. The specific surface area was calculated using the BET method. The porosity evaluation was done via Barrett–Joyner–Halenda (BJH) models, from the desorption branch, considering the presence of slit pores. The total pore volume obtained by Gurvitch method was determined from nitrogen adsorption data at relative pressure of 0.95. The specific surface area for Mt sample was: SN_2 = 27 ± 5 m^2/g [26].

The differential thermogravimetric analyses (DTA) were performed on a 35 mg sample in a Shimadzu instrument (DTA-50), from room temperature to 800 °C at a heating rate of 10 °C/min, in N_2 atmosphere.

Semioriented samples were maintained at relative humidity (rh) of 0.47 for 48 h and then analyzed by XRD. The X-ray diffraction patterns ((0 0 1) reflection peak), collected from 3° to 13° (2θ), were obtained using a Philips 3020 with Cu Kα, 30 mA and 40 kV, counting time of 10 s/step.