



Research paper

Adsorption of two fungicides on natural clays of Morocco

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ABSTRACT

North of Morocco is becoming one of suppliers of tourism sites and agricultural products for Europe. Thus, environmental risks from this region are important for the future of these activities. The presence of pesticides in soils and waters can become a serious environmental problem. Clay minerals can be used for mitigation of this problem. In this work, the adsorption of two fungicides, metalaxyl and tricyclazole, on natural Northern Moroccan clays was investigated using the batch equilibration method and several techniques, such as, X-ray diffraction (XRD), thermal analysis (TGA/DSC), and surface area measurement (BET) were used for clay characterization. The data from kinetic and adsorption studies were fitted to different models. The adsorption kinetics of these fungicides followed a pseudo-second-order model. Adsorption data, higher for metalaxyl than for tricyclazole, were fitted the Freundlich model. A natural stevensite was the clay with the highest adsorption capacities for both fungicides.

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1. Introduction

The widespread use and disposal of pesticides in agricultural activities can produce environmental contamination of surface and ground-water with a possible health risk, due to their potential toxic, carcinogenic and mutagenic effects (Zhao et al., 2008). Trace levels of pesticide residues can be present in soil, water, air and sometimes food, and may result in harmful effects on human and environmental health (Amweg et al., 2005). Besides, these polluted soil components can be present in aerosols suspended in the air during long periods of time and over long distances. Silicates from the Sahara have been detected in North Europe and America (Iuga et al., 2010). The presence of these silicates with organic pollutants in these aerosols may affect atmospheric and stratospheric chemical reactions and their impact on Climate Change may be enhanced by the high levels of solar radiation (Iuga et al., 2010). The increasing presence of pesticides in natural ecosystems (Sánchez-González et al., 2013) has stimulated research on sorbent materials (Zheng et al., 2010; Chaara et al., 2011) which can be used to remediate and prevent soil and water contamination (Park et al., 2014; Stipicevic et al., 2014; Ouali et al., 2015).

Immobilization processes occurring in a soil are of great environmental importance because they may lead to a considerable reduction in the bioavailability of organic pollutants, which may be bound to soil constituents by physical forces or chemical reactions of varying strength. These naturally occurring processes are believed to result in pollutant detoxification and have long been suggested for decontamination (Bollag et al., 2002). However despite the role that soil plays as a barrier to attenuate the wide spread of pollutants, different systems have been sought, which may help in pollutant detoxification/mitigation: biological

degradation using selected microorganisms (Chelinho et al., 2010; Chen et al., 2011), or chemical pathways such as electrochemical oxidation, photocatalytic degradation, or advanced oxidation processes (Lu et al., 2011; Liu et al., 2012; Wang et al., 2012). Another approach is based on the use of physical barriers to increase pollutant trapping, among which the use of natural clays has been proposed because this natural material is highly compatible with environmental policies (Gonzalez-Pradas et al., 1999; Stringfellow et al., 2011; Sánchez-Jiménez et al., 2012). In order to improve the ability of clays to retain pollutants, modifications have been incorporated to obtain other environmentally compatible products (Rodríguez-Cruz et al., 2008; Suciú et al., 2011).

In soils the fractions with the highest adsorption capacity for pollutants are the clay fraction along with organic matter. Clay minerals, especially the smectite family, have received considerable attention owing to their physicochemical properties (Bergaya et al., 2006) and high capacity to retain organic compounds. Phyllosilicates are a very abundant group in soils. They have a layered structure and many physicochemical properties of these minerals depend on cation substitutions in the tetrahedral or octahedral sheets, since they confer a residual negative charge to the sheets, which must be compensated by cations in the interlayer space. Because of their layered structure, high specific surface and natural occurrence, clay minerals play a major role in the adsorption of pollutants in soils, especially organic compounds.

Sediments in the North of Morocco have interesting amounts of clay mineral deposits especially in the extreme West of the Riff mountains ridge, in the area of Tanger-Tetuan. The main uses of these deposits are as construction materials. In fact, only the region of Tetuan produces more than the 45% of the total clay materials for construction in Morocco. One Moroccan clay with special properties and highly used

in Cosmetic and Health treatments is the one called locally Rhassoul, whose deposit is located in the east side of the middle-Atlas mountains of Morocco. This clay has been identified as stevensite (Chahi et al., 1999). Moreover, the agricultural use in this area is very intensive, which can increase enormously the risk of concentration of pesticides. This issue affects Public Health because this pollution can reach the water-table of drinking and irrigation water, and go into the human cycle. This point has also an international dimension because the North of Morocco is becoming one of the main suppliers of agricultural products to Europe. Besides, this region is becoming highly attractive for tourism and the environmental risks may affect this economic activity (El Bakouri et al., 2007; Azejjel et al., 2010). Therefore, a deep knowledge of the clay minerals and their interactions with pollutants in this area of North of Morocco is essential for Moroccan and European interests and is necessary in order to prevent Public Health risks of soil contamination and for exploring new strategies for a sustainable development of this area.

In this study, metalaxyl and tricyclazole were chosen as model compounds of pollutants in water owing to their generalized use to control fungal diseases in a variety of crops. The adsorption of both fungicides, with different physical–chemical properties, onto several samples of Moroccan clay minerals was assessed. One of the aims of this work is to use natural clays for ecological applications hence the use of surfactants with these minerals was not considered in this work to avoid additional pollution. In addition, relationships between pesticide retention and clay structure, identified by using a wide array of instrumental techniques, have been proposed.

2. Materials and methods

2.1. Natural clays samples

Four clays with different characteristics from various locations in Northern Morocco (30 cm-depth) were selected: white Bentonite (BT) from Segangane-Nador (57.4%, 24.7% and 12.3% of clay, silt and sand, respectively), Ghassoul clay (ST) from Missouri-Meknes (mainly stevensite), a sample from the Dchiriyine zone in Tetouan (CTe) (Azejjel et al., 2009) and a sample from Targuist (CTa) (31.3%, 29.6% and 35.9% clay, silt and sand, respectively).

2.2. Pesticides

Two organic molecules were evaluated for the study of adsorption onto clays: metalaxyl and tricyclazole (Fig. 1). Metalaxyl (methyl N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alaninate) is a phenylamide fungicide that inhibits the protein synthesis in fungi, by interference with the synthesis of ribosomal RNA. Tricyclazole (5-methyl-1,2,4-triazolo[3,4-b][1,3]benzothiazole) is a systemic fungicide which acts as

melanin biosynthesis inhibitor (Tomlin, 2003). Standards of both pesticides (>98% purity, Dr. Ehrenstorfer, Germany) were employed in the adsorption study. Their octanol/water partition coefficients ($\log K_{ow}$) are 1.75 and 1.40, and their solubility in water 8.4 and 1.6 mg L⁻¹ for metalaxyl and tricyclazole, respectively, with greater water solubility for metalaxyl, in accordance with its higher content of oxygenated polar groups (Fig. 1).

2.3. Analytical methods

The pH of these raw samples was measured in water/clay dispersions, ratio 1:2.5 (w:v). The organic carbon (OC) content was determined by a modified Walkley & Black method (Mingorance et al., 2007). The cation exchange capacity (CEC) was determined by a method based on the triethylene-tetramine-Cu complex (Meier and Kahr, 1999). The measurement of the specific clay surface was carried out with a "Micromeritics ASAP 2010" analyser that uses the process of multilayer adsorption of nitrogen gas (99.98% purity) at 77 K according to the BET theory (Brunauer et al., 1938), based on determining the amount of gas needed to set a monolayer on the solid surface. All water and gases molecules deposited on the sample surface were evacuated, by degassing overnight at reduced pressure ($<10^{-4}$ Torr) and 120 °C. The chemical composition of clay samples were characterized by X-ray fluorescence (XRF), using a S4 Pioneer BRUKER analyser, after drying the samples at 60 °C for 48 h, and grinding them into a fine powder. The thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) studies were performed in a Shimadzu 50 H analyser, using Al₂O₃ as reference, with a heating rate of 20 °C min⁻¹ in air atmosphere. The transmission electron-microscopy (TEM) was performed with a Phillips CM-20 microscope, operated at 200 kV and equipped with a device for analytical electron microscopy (EDAX). The powder X-ray diffraction (XRD) studies were performed by using a Siemens D-5000 diffractometer with Ni filter and the K α radiation of Cu ($\lambda = 1.544 \text{ \AA}$) in the theta range of 3–70° with steps of 0.017° and 19.7 s of counting time per step and a slit width of 0.25°. These diffractograms were recorded as disordered powder sample from raw material and purified samples. The XRD profiles of purified samples were obtained also as oriented aggregate, after treatment with ethylene glycol and after a thermal treatment of 550 °C. For the purification process, samples were sieved at <2 mm size and suspended in water. An initial treatment with acetic acid was performed to minimize the amount of carbonates, followed by further washings with deionized water; then the sample was suspended in water for 20 min, dispersed with sodium hexametaphosphate, treated in a ultrasonic bath (5 min) and repeated siphoning of the dispersed material (settling 7 h and 22 min at 22 °C, siphoning the supernatant upper 10 cm from atmosphere interface and the bottom residue separated) and the liquid phase was centrifuged. The remaining solid was considered a <2 μm fraction that after drying constituted approximately 20% of the initial sample. For distinguishing the phyllosilicate composition, this purified sample was treated under ethylene glycol vapours during 24 h: After analysing this sample by XRD, the sample was treated at 550 °C during 2 h and a final XRD analysis was performed.

The concentration of fungicides in the supernatants was determined by high performance liquid chromatography with diode array detector (HPLC-DAD) (Agilent Series). A 10- μL sample, after filtration by GHP Acrodisc filters (0.45 μm), was injected into a Zorbax RX C8 column (15 cm \times 2.1 mm i.d., 5 μm \varnothing), protected by a guard column Eclipse XDB-C8 (1.25 cm \times 2.1 mm i.d., 5 μm \varnothing) at a flow rate 0.2 mL min⁻¹, the mobile phase consisting of a 50:50 (v:v) mixture of acetonitrile/water and wavelength detection of 220 nm for metalaxyl and 200 nm for tricyclazole. Calibration was performed by triplicate injection of standard solutions between 0.25 and 8 mg L⁻¹ ($R^2 = 0.999$). With these conditions, the retention times for metalaxyl and tricyclazole were 4.3 and 3.2 min, respectively.

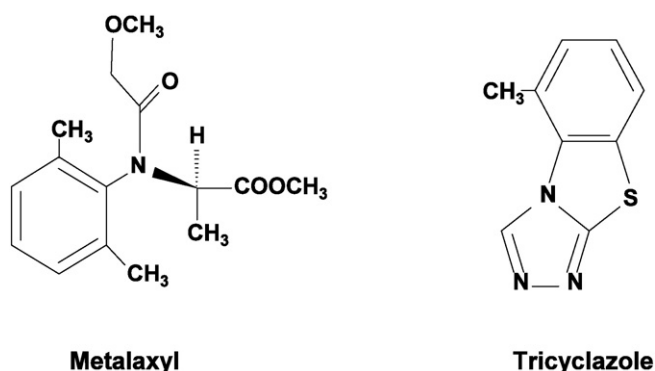


Fig. 1. Chemical structure of metalaxyl and tricyclazole.

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