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Research paper

Fe-pillared clay mineral-based formulations of imazaquin for reduced leaching in soil

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ABSTRACT

Slow release formulations of the herbicide imazaquin (2-(4-isopropyl-4-methyl-5-oxo-4,5-dihydro-1H-imidazol-2-yl)quinoline-3-carboxylic acid) were prepared by its adsorption on Fe-pillared clay minerals (Fe PILCs). Fe PILCs were synthesized by the reaction of Na^+-montmorillonite (SWy-2) with base-hydrolyzed solutions of Fe and Al. The Fe/(Fe + Al) ratios used were 0, 0.05, 0.15 and 0.50. Fe PILCs showed basal spacing values of 5.2 and 1.8 nm which were due to iron clusters between delaminated clay layers, and intercalated aluminum polyoxocations, respectively. As iron content increased, the pillaring process yielded PILC with lower microporosity and larger mesoporosity. The affinity of imazaquin on Fe PILCs was very high relative to Al PILC, as revealed in its higher herbicide adsorption values and lower desorption percents. Competitive adsorption of anions such as sulfate, phosphate and chloride provided evidence of formation of inner sphere complexes of imazaquin on Fe PILCs. Slow release formulations were prepared by enhanced adsorption of the herbicide from imazaquin–cyclodextrin (CD) complexes in solution. CDs were able to enhance up to 8.5-fold the solubility of imazaquin, by the formation of inclusion complexes where the quinolinic moiety of the herbicide was partially trapped within the CD cavity. Release of the herbicide in sandy soil was about 1/2-fold lower from Fe PILC formulations relative to the commercial formulation.

1. Introduction

Herbicides are applied to impede the growth of weeds and improve the yield of crops. However, only a part of the applied amount reaches its target whereas the rest remains either attached to the soil colloids or undergoes degradation and transfer processes such as migration of the herbicide to surface and groundwater, which has been reported to be one of the main sources of polluted waters (Finizio et al., 2011; Metcalfe et al., 2011). To minimize this effect, research has focused in the last decades on the development of slow release formulations (SRFs) of herbicides that permit to decrease the losses of the used amounts but to achieve good bioactivity, thus providing safer environmental formulations (Fernández-Urrusono et al., 2000; Sopeña et al., 2005; Undabeytia et al., 2000, 2003, 2010).

Clay minerals have been studied as good candidates for SRF because of their good adsorbent properties in addition to their abundance and low-cost. Most of the studies were performed on montmorillonite (Mt) whose surface was modified previously from hydrophilic to hydrophobic by pre-adsorbing organic cations, which were further used for enhanced adsorption of the active ingredient. In general, high adsorption is usually correlated with slow release properties (Mishael et al., 2003). Recently, hydrotalcites were used based on the same principle, but using organic anions (Zhenlan et al., 2009). Other clay mineral-based approaches were trapping of the herbicide by coagulation of delaminated clay mineral layers (Nennemann et al., 2001a), adsorption after previous thermal treatment (Bojemueller et al., 2001), bentonite polymer gels (Li et al., 2009), and sepiolite gels (Maqueda et al., 2008, 2009).

Pillared clay minerals (PILCs) were proved very effective in the adsorption of herbicides and organic contaminants due to geometrical compatibility between the structural pores and molecular dimensions of the chemicals, in addition to their specific interactions with the pillars and layers of the clay mineral (Cheknane et al., 2010). Adsorption capacity of PILC was used for the preparation of SRF of herbicides (Gerstl et al., 1998; Nennemann et al., 2001b).

Imazaquin (IMZQ) is a selective imidazolinone herbicide used for broad-spectrum weed control in legume crops (Ahrens, 1994). IMZQ has an acidic carboxyl and a basic quinoline functional group with pKa values of 3.8, and 2.0, respectively (Regitano et al., 2005). Therefore, it exists as an anion at typical soil pH values, increasing its risk for leaching down the soil profile. A PILC formulation was designed to reduce its leaching in soil (Polubesova et al., 2002). In the current work, SRFs of the herbicide imazaquin were designed based on PILC prepared from hydrolyzed iron solutions instead. Imidazolinone herbicides are known to form complexes with transition metals (Erre et al., 1998). Imazaquin adsorption on soils with different physicochemical properties was greater on the soil containing higher amorphous iron oxide content

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(Undabeytia et al., 2004). This pointed to the formation of stronger complexes with iron over other elements as aluminum, and hence, enhanced imazaquin adsorption and stronger retention on Fe PILC. The validity of this approach for the preparation of SRF was examined in the current paper.

In general, the active ingredient loading on clay-based formulations is limited by the herbicide solubility, which prevents further adsorption. Cyclodextrins (CDs) are cyclic oligosaccharides produced by the enzymatic breakdown of starch by bacteria. These molecules have a toroidal shape, with a hydrophobic interior cavity and hydrophilic faces (Szejtli, 1998). The ability of these molecules to form inclusion complexes with non-polar molecules has been exploited in the pharmaceutical industry as a solubility enhancement agent (Bikiaris, 2011). Environmental applications for subsurface soil remediation of organics have started to be described based on the very poor CD adsorption on soil colloids (Fenyvesi et al., 2011; Villaverde et al., 2005). Therefore, the active ingredient content of the PILC formulations can be increased by performing adsorption of the herbicide in solution from CD inclusion complexes. The herbicide will be solubilized and adsorbed on the clay mineral whereas the CD will remain mostly in solution.

The objectives of this work were: (i) to prepare Fe PILCs as adsorbents for the preparation of SRF; (ii) to study the formation of inclusion complexes of IMZQ with CD; (iii) to prepare slow release formulations from CD–IMZQ solutions; and finally (iv) to test these formulations for slow release.

2. Materials and methods

2.1. Materials

Wyoming Na^+–Mt (SWy-2) was obtained from the Source Clays Repository of The Clay Minerals Society (Columbia, MO) (cation exchange capacity 0.8 mmol/g). Al $(NO)_3{\cdot}9H_2O$, $FeCl_3{\cdot}6H_2O$, NaCl, Na_2SO_4, Na_3PO_4, H_3PO_4 and NaOH were purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). HPLC grade-acetonitrile was obtained from Teknokroma S.A. (Barcelona, Spain). Imazaquin (IMZQ 97% purity) was supplied by Sigma-Aldrich and its commercial formulation (Scepter, 180 g a.i. L^{-1}) by Agan Makteshim (Lérida, Spain). Cyclodextrins (CDs) were purchased from Cyclolab (Budapest, Hungary). CDs employed were: α-CD, β-CD, hydroxypropyl-β-CD (HPβ), and randomly methylated-β-CD (RAMEβ). Fig. 1 shows the structural formulas of IMZQ and CD.

The upper part (0–20 cm) of sandy soil classified as Typic Xeropsamment was collected, and passed through a 2 mm sieve before use. This soil has a pH of 8.9 and 0.79% of organic matter (more detailed physicochemical properties are given in Undabeytia et al., 2012).

2.2. Preparation of pillared clay minerals

Aluminum nitrate and iron chloride solutions in several Fe/(Al + Fe) molar ratios (0, 0.05, 0.15, 0.5) were hydrolyzed by titration with 0.4 M NaOH under nitrogen atmosphere. The Al/OH molar ratio was 2.0. These pillaring solutions were aged for 7 days. Then, 10 g of clay mineral was dispersed in 250 mL water, and the pillaring solutions in a ratio of 10 mmol (Fe + Al)/g clay mineral were added slowly with a peristaltic pump under nitrogen atmosphere. The final clay mineral content was 1% (w:w). The dispersions were under shaking for 24 h, followed by centrifuging, removal of chloride by dialysis, and dry-freezing. Finally, the powder clay minerals were heated for 3 h at 300 °C under nitrogen atmosphere.

A nomenclature was used for the PILCs where the first letters, Al or Fe, respectively indicated the absence or presence of iron in the pillaring solutions, and the following numbers indicated the used Fe/(Al + Fe) ratio.

2.3. Characterization of PILC

The chemical composition of the PILC was determined by X-ray fluorescence (PANalytical Model Axios).

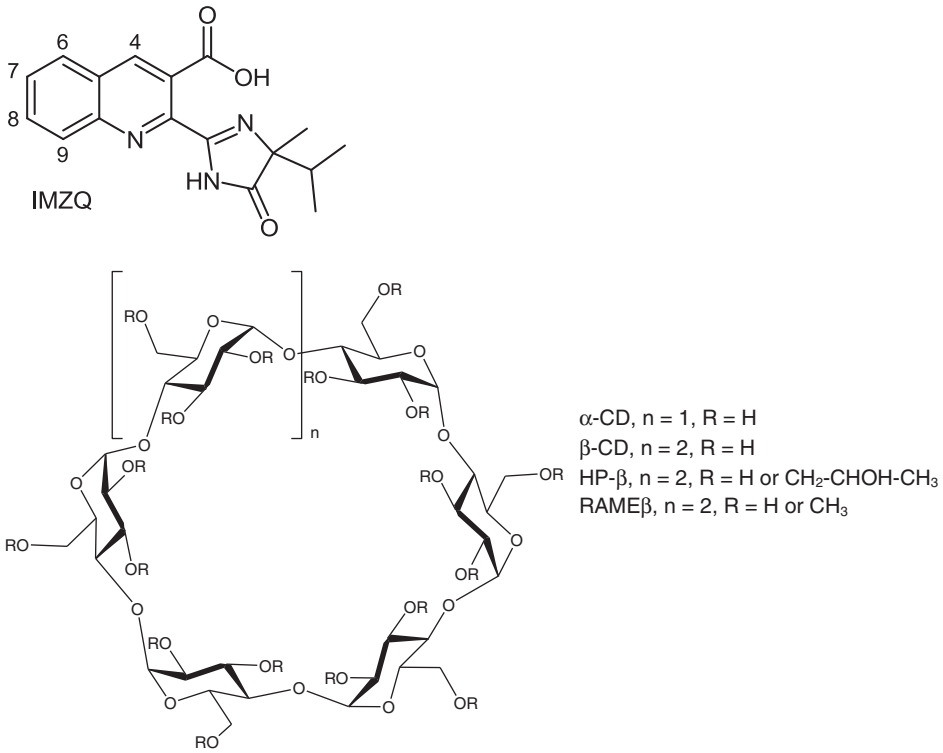

Fig. 1. Structural formulas of the herbicide imazaquin and cyclodextrins.