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BISPYRIBAC NANOPESTICIDES FROM ANIONIC AND ALKYLAMMONIUM CATIONIC CLAYS FOR MINIMIZING WATER ENVIRONMENTAL RISKS

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The development of new formulations based on clays as smart delivery systems or nanopesticides has become an interesting strategy for decreasing the environmental impact of pesticides [1-3]. Layered double hydroxides (LDHs) or anionic clays are especially convenient as host materials for anionic or acid pesticides to decrease their soil leaching losses, which are often very high for this type of pesticides, particularly if they have high water solubility [4]. Alkylammonium cationic clays have also been shown as good carriers for pesticides in controlled release formulations [3,5]. We prepared and compared nanopesticide formulations of a very water soluble anionic herbicide, bispyribac (BIS), as LDH and as alkylammonium clay complexes, whose water and soil behaviour were lab-tested, as smart delivery systems to minimize their surface and ground water impact.

The initial materials were LDH, lab-synthesized and calcined at 500°C (LDH500), and alkylammonium Cloisite 10A (Clo10A) from BYK and supply by Comindex SA. The adsorption of bispyribac on LDH500 and Clo10A was firstly assayed. The LDH-BIS complex was prepared by regeneration of LDH500 in aqueous solution containing herbicide. The Clo-BIS complexes (20% w/w) were prepared in three ways: (i) ground mixing (GM); (ii) weak complex (WC) and (iii) strong complex (SC)³. The characterization of the LDH-BIS and Clo-BIS complexes were done by XRD, SEM and FTIR spectroscopy. The bispyribac slow release in water and the bispyribac leaching out from the soil column experiments were designed to compare the diverse nanopesticide complexes versus its technical and commercial products (Nominee 400SC).

The L-type isotherm showed that bispyribac adsorbed on both clays by specific mechanism and fitting to Langmuir model rendered a monolayer capacity much larger for LDH500 ($Q_m=1.3$ mmol/g) than for Clo10A ($Q_m=0.2$ mmol/g). The XRD of LDH-BIS complex showed that layered structure was recovered and herbicide was mainly in the interlayer with a basal spacing of 22.4 Å as an anion (~25% of AEC), besides some carbonate and nitrate, as revealed by FT-IR. The XRD of Clo-BIS complexes showed that GM displayed an unchanged Clo10A (19 Å) basal spacing, whereas the other WC and SC complexes showed an increase and broadening of d_{001} around 21 Å indicating a disordered with different interlayering grade of bispyribac. The FT-IR spectra confirmed the presence of bispyribac as anion in all the complexes. The water release profiles showed the technical product and the Clo10A-BIS GM released immediately 98% and 100% of their initial herbicide content, whereas the LDH-BIS, and Clo10A-BIS SC and WC released immediately 18, 23 and 65% reaching, after 120 h 68, 25 and 75%, thus displaying slow release profiles. The SC complex Clo10A-BIS could not be appropriated because of its very low final release. The soil column leaching studies revealed important differences among the diverse nanopesticides and with technical and commercial products. Those differences, as the corresponding water release profiles, were related with structure and interaction mechanism of bispyribac in the complexes. These results show that, combining a selection of carriers with diverse preparation modes, the resulting nanopesticides can offer a wide range of leaching risk minimization strategies.

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