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Title : SYNTHESIS AND CONTROLLED RELEASE CHARACTERIZATION OF ZINC-ALUMINIUM-HERBICIDE HYBRID NANOMATERIALS

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In the modern agriculture, various agrochemicals such as pesticides, herbicides, and plant growth regulators are widely used for effective pest management and ensuring optimum crop yield. Most herbicide formulations deliver the bulk of the active agents that can be readily released to the environment. This phenomenon leads to pesticide residues in the food chain, and this, in turn, has adverse effects in humans including carcinogenic, mutagenic, and teratogenic effects. As a solution for this, we developed a controlled release agrochemical in which the herbicide is embedded into a matrix that can be released in a controlled condition manner. This study aimed at the synthesis of a new controlled release of herbicides, namely 2-methyl-4-chlorophenoxy acetates (MCPA), 2,4,5-trichlorophenoxybutyrate (TBA) and 3,4-dicholorophenoxy acetates(3,4D) through intercalation of the herbicides into zinc-aluminium-layered double hydroxide by self-assembly and anion-exchange method. The release of herbicides into various aqueous media and the kinetic profile were also studied after the successful intercalation of the herbicides at their optimum condition. In this study, a phase pure, well-ordered nanocomposite was successfully synthesized using both self-assembly and anion-exchange method. Upon the successful intercalation of all the three herbicides into LDH by self-assembly method,the expansion of basal spacing from 8.9 Å in the Zn-Al-layered double hydroxide to 19.0, 28.2 and 18.7 Å in zinc- aluminium-LDH-2-methyl-4-chlorophenoxy acetates (ZAM), zinc-aluminium -LDH -2,4,5-trichlorophenoxybutyrate (ZAT) and zinc-aluminium-LDH-3,4 -dicholorophenoxy acetates (ZAD) nanocomposites could be observed, respectively. The basal spacing for the nanocomposites obtained by the anion exchange method was found to be 19.0, 23.3 and 19.0 Å for ZAM, ZAT and ZAD, respectively. All the nanocomposites synthesized in this work are of Type IV which is mesoporous type of material containing 48.0 % (w/w%), 54.5 % (w/w%) and 53.5 % (w/w%) of 2-methyl-4-chlorophenoxy acetates, 2,4,5-trichlorophenoxybutyrate and 3,4-dicholorophenoxy acetates, respectively. Release of all anions into various aqueous solutions containing phosphate, sulphate and nitrate anion increased with contact time in the order of phosphate > sulphate > nitrate. This work suggests that the affinity of incoming anion towards the LDHs layer was determine by the charge density of the incoming anion. The release profiles of the three anions into the aqueous solution were found to follow the pseudo-second order kinetic model. This study shows that the zinc-aluminium-layered double hydroxide can be used as a host for controlled release formulation of agrochemicals. Besides single intercalation, the dual intercalation of MCPA and 3,4D (ZAMDX), MCPA and TBA (ZAMTX) as well as TBA and 3,4D (ZADTX) were attempted with Zn-Al-LDH host. All the dual intercalation was synthesized using 0.1 M solution of herbicides. The well-ordered, layered nanohybrid basal spacing was expanded from 8.9 Å in LDH to 19.3 Å for ZAMDX, 23.1 Å for ZAMTX and 20.0 Å for ZADTX, respectively. The release of both anions from the nanohybirds (ZAMDX, ZAMTX and ZADTX) into an aqueous solution of Na_2SO_4 was found to be governed by pseudo second-order kinetics.