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Ab initio Investigation of Layered Double Hydroxides with Intercalated Herbicides

Pedro Ivo R. Moraes, Sérgio R. Tavares, Viviane S. Vaiss, Alexandre A. Leitão

Departamento de Química, Universidade Federal de Juiz de Fora, Juiz de Fora, MG 36036-330, Brazil

Abstract: Layered double hydroxides (LDHs) or hydrotalcite-like compounds exist either as naturally occurring minerals or as synthesized materials by low-cost synthesis methods. LDHs consist of positively charged metal hydroxide layers having the composition $[M^{2+}_{1-x}\ M^{3+}_{x}(OH)_2]^{x+}[A^{m-}_{x/m}\cdot nH_2O]$ where M^{2+} and M^{3+} are divalent and trivalent cations, respectively. The value of x is the molar fraction and can vary between 0.2 and 0.33, and A^{m-} is the interlayer anion [1]. The contamination of soils and ground water by pesticides is a consequence of their increasing use in modern agriculture. The contamination of ground and surface water reservoirs by acid pesticides is even higher, because their anionic form predominates under the pH conditions of the soil and of the water environments, thus being weakly retained in the soil [2]. All calculations were performed using the codes available in the Quantum-Espresso package [3], which implements the DFT [4] framework using a plane-wave bases set, periodic boundary conditions, and pseudopotentials. We used the generalized gradient approximation, GGA-PW91 [5] for the exchange-correlation (XC) functional, and Vanderbilt ultrasoft pseudopotentials [6] were also used to describe the ion cores. The investigated herbicides are 2,4D (2,4-dichlorophenoxyacetic acid) and MCPA (4-chloro-2-methylphenoxyacetic acid) intercalated in Mg-Al and Zn-Al LDH with x = 0.33 for both. The supercells used for their constructions were $\left(2\sqrt{3}\,x\,2\sqrt{3}\right)R30^{o}$ [7], with each supercell having two intercalated herbicides in their anionic forms. The structures were fully optimized and their basal spacings calculated for [Mg-Al-2,4D], [Mg-Al-MCPA], [Zn-Al-2,4-D] and [Zn-Al-MCPA] were 19.10 Å, 19.20 Å, 19.00 Å and 19.08 Å, respectively. These results present a good agreement with the experimental values [8-9]. The electronic density difference plots were made for the LDHs in order to study the interactions between the layers, the anions, and the hydration water molecules. We can see a strong interaction between the anion carboxyl group and the layer hydroxyl groups, and also with the water molecules. We can also observe the interaction between the layer hydroxyl groups and the water molecules. The interactions between the interlayer anions are weak. The projected density of states (pDOS) shows that, for each structure, the basic site is the intercalated anion. The Bader analysis was also performed to verify the atomic charge distribution in the LDH structure. The anion has the same charge in each structure, while the charge is different in the layer for Mg (1.75 *e)* and Zn (1.36 *e)*. The Bader charges of the layer oxygen atoms were also distinct for the Mg-Al

layer and forthe Zn-Al layer, being -1.95 *e* and -1.82 *e*, respectively. This work is still under development.

Key-words: Layered Double Hydroxides, LDH, Herbicide, DFT

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