Adsorption of Tyrosinase onto Montmorillonite as Influenced by Hydroxyaluminum Coatings

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Abstract: In soil environments, the surfaces of clay minerals are often coated with hydrolytic products of Al. However, limited information is available on the effect of hydroxyaluminum coatings on the interlayering of enzymes for montmorillonite. The objective of this study was to compare the adsorption of tyrosinase onto montmorillonite as influenced by levels of hydroxyaluminum coatings. Tyrosinase is one of the strongest catalysts in the transformation of phenolic compounds. Adsorption of tyrosinase onto Ca-montmorillonite (Ca-Mte) and different hydroxyaluminum-montmorillonite complexes ($Al(OH)_x$-Mte), containing 1.0, 2.5 and 5.0 mmol coated Al/g clay, was studied both in the absence and in the presence of a phosphate buffer at pH 6.5 and 25 ° C. Except for Ca-Mte in the absence of phosphate where the adsorption isotherm was of C type (linear), the adsorption isotherms were of L type (Langmuir). More tyrosinase molecules were adsorbed onto Ca-Mte than onto the Al $(OH)_x$-Mte complexes, both in the absence and in the presence of phosphate. This indicated the easy accessibility of the enzyme to the uncoated Ca-Mte surfaces. The presence of phosphate did not significantly affect the amount of tyrosinase adsorbed onto Ca-Mte, but substantially reduced the adsorption of tyrosinase onto $Al(OH)_x$-Mte complexes. The higher the level of hydroxyaluminum coatings, the lower the amount of tyrosinase was adsorbed. Because of their affinity to the aluminous surfaces, phosphate ions evidently competed strongly with tyrosinase for $Al(OH)_x$-Mte complexes adsorption sites. The intercalation of tyrosinase by Ca-Mte was indicated by the increased d-spacing of the complex as the amount of the enzyme adsorbed increased. The infrared spectra of tyrosinase-Ca-Mte complex showed that the amide II band of tyrosinase at 1540 cm^{-1} was practically unaffected by adsorption. The amide I band at 1654 cm^{-1} was shifted toward a higher frequency, indicating a slight perturbation in the protein conformation. This perturbation became more noticeable in the presence of $Al(OH)_x$-Mte complexes. The data indicated that hydroxyaluminum coatings play an important role in retarding the adsorption of tyrosinase by montmorillonite, and phosphate effectively competes with tyrosinase for the adsorption sites on $Al(OH)_x$-Mte complexes.

Key Words: Adsorption • Clay minerals • Enzymes • Hydroxyaluminum-montmorillonite complex • Interlayering • Tyrosinase

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