FREEZE-DRYED HYDROGEL was prepared from a colloidal suspension of chitosan and xanthan gum blend in order to encapsulate enzyme (firefly luciferase), and the release behavior of the enzyme from the prepared hydrogels was investigated. Selected amount of luciferase was simply mixed into the original polymer solution, and was stabilized in the resultant freeze-dried samples. The encapsulated enzymes were released from the rehydrated dry samples (hydrogel) at moderate rate. Prepared samples were found to be sensitive to the pH of the solution, that is, the release rate of the enzyme was larger in pH=6 than in pH=8. It was found that the addition of the montmorillonite nanoclay (MMT) was interesting pathway that could alter the enzyme release behaviors. The release rate of protein from the sample prepared via the MMT addition was obviously lower than that of the sample without containing the nanoclay. It was suggested by the small angle X-ray scattering measurements that the modification of the polymeric network formation caused by the MMT addition (it was also caused by changing the freezing condition during freeze-drying) was influential to the protein binding properties in the hydrogels that related to the release behavior. Enzymatic activities of both the stabilized and released enzyme were fairly confirmed, suggesting that the present hydrogel formulation is a useful support for encapsulating bio-active substances such as enzymes.