Effect of layer charge and charge distribution on the formation of smectite-chitosan nanocomposites

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Intercalation of organic compounds in smectites yields nanocomposites which have attracted intense research interest because they are high added value materials which find novel applications in a variety of uses. Chitosan based nanocomposites display structural and functional properties which if combined with the biocompatibility and biodegradability of the biopolymer may be of great interest in nutrition, cosmetics, water treatment, tissue engineering and drug delivery among other purposes [1]. In the present study, SAz-1 (high charge) and SWy-1 (low charge) montmorillonites, SBId-1 (low charge) beidellite and NAu-1 (high charge) nontronite obtained from the Source Clays Repository of the CMS, were selected based on their layer charge magnitude and charge distribution. The samples were classified according to the layer charge of the smectites, according to Christidis et al. (2006) [2]. Chitosan based nanocomposites were prepared with the addition of chitosan solutions to < 2μm homoionic Na^+ - smectite clay fractions to obtain nanocomposites with initial chitosan-smectite ratios of 0.25:1, 0.5:1, 1:1, 2:1, 5:1 and 10:1 respectively. The nanocomposites were examined by XRD. In addition, adsorption isotherms of the chitosan-smectite nanocomposites were prepared.

The intercalation of chitosan in the smectite interlayer was monitored by the migration of the 001 diffraction maximum towards lower angles and was characterized by decrease in the intensity of the basal reflections with increasing chitosan-clay ratio. At low chitosan loadings SAz-1 displayed highest (15.4 Å) and SWy-1 lowest d_{001} spacing (13.2 Å) with the beidellite and nontronite displaying intermediate d_{001} spacings (~15 Å). At high chitosan loadings SWy-1 displayed maximum d001-spacing (21.2 Å), whereas in SAz-1 was barely modified (d_{001}=15.9 Å). Tetrahedral substitution led to a broad basal reflection with two diffraction maxima at 15.4 and 19 Å due to inhomogeneous chitosan intercalation in beidellite and nontronite layers, whereas homogeneous intercalation was observed for low- and high- charge montmorillonites. The XRD results are in accordance with the adsorption isotherms of chitosan on the different smectites.

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[1] Darder M., Aranda P., Ruiz-Hitzky E. (2012). Chitosan-Clay Bio-Nanocomposites. In L. Avérous and E. Pollet (eds.), Environmental Silicate Nano-Biocomposites, Green Energy and Technology, DOI: 10.1007/978-1-4471-4108-2, 14. Springer-Verlag, London.

[2] Christidis G.E., Blum A.E., Eberl D.D. (2006). Influence of layer charge and charge distribution of smectites on the flow behaviour and swelling of bentonites. Applied Clay Science, 34, pp. 125-138.