OC 10 - Molecularly Imprinted Chitosan-Genipin Hydrogels with Recognition Capacity towards PCB Analogues

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This investigation aimed to develop molecularly imprinted hydrogels (MIH) with stereochemical memory towards o-xylene, taken as an analogue of PCB contaminants. To this end, chitosan was chemically cross-linked with genipin, a natural compound derived from the fruit of Gardenia jasminoides. The kinetics of gel formation of chitosan-genipin hydrogels was probed by dynamic oscillatory rheology as a function of chitosan concentration and reaction stoichiometry (R). Second order kinetics was found for the dependence of the critical gel time with chitosan concentration. The apparent activation energy of the gel formation process was 67.16 ± 4 kJ/mol. During the preparation of the MIHs, retention of o-xylene within the gel network and its subsequent removal under aqueous acid treatment, were probed by FTIR and GC-MS chromatography, respectively. GC-MS was also used to measure the amount of adsorbed analyte by MIHs. Adsorption of o-xylene by MIHs was slightly greater than their corresponding control hydrogels, and maximal adsorption seemed to occur for MIHs with R = 0.25. Scatchard analysis showed that these MIHs had heterogeneous binding sites, namely, with high and low affinity (Kd=7.7×10^{-8} and 1.8×10^{-6} mol/L, respectively) and hence with varying adsorption capacity. Chitosan/genipin MIHs exhibited adsorption affinity not only towards o-xylene, but also towards p- and m-xylene isomers and to a much lessen extent towards 2-fluorotoluene. Control hydrogels also displayed some affinity towards xylene analytes, but always less than that shown by MIHs. These results were rationalized as the consequence of the creation of sites of specific recognition in molecularly imprinted chitosan-genipin gel networks, a result in agreement with previous studies undertaken in chitosan/glutaraldehyde MIHs. The approach developed in this study is thought to be useful in the development of new advanced materials for identification and/or separation of PCBs and other specific molecules in several fields of application.