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Novel crosslinked gels with starch derivatives. Polymer-water interactions. Applications in waste water treatment.

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SUMMARY: Crosslinked polymers containing starch have been used for the recovery of various pollutants from aqueous solutions. These polymers have been prepared by reticulation of starch-enriched flour using epichlorohydrin as crosslinking agent. Several studies (kinetics, time, concentration, role of crosslinking agent) are presented here. The results show that these polymers exhibit high sorption capacities toward substituted phenol derivatives. The mechanism of sorption is both physical and steric adsorption in the polymer network and/or the formation of hydrogen bond and hydrophobic interactions.

Introduction

Phenols derivatives are the subject of increasing interest in recent years[1-5)]. These toxic compounds are products of many industrial processes and they may be found in trace in industrial waste water. Therefore, it would be advantageous to have adsorbent resins that are able to totally eliminate them. Crosslinked polymers[1,2,6,7)] constitute an interesting class of materials that have found a variety of applications, such as in waste water treatment.

In this work, we propose the use of insoluble crosslinked starch-polymers as adsorbents resins to sorb aromatic pollutants. These polymers have been prepared by polymerization of starch-enriched flour using epichlorohydrin as a crosslinking agent (scheme 1). Details of the materials and the synthetic procedure have already been described[8)]. Fig. 1 shows the CPMAS spectra of starch-enriched flour where it can be seen the classic peaks of starch and peaks due to impurities, and the CPMAS spectra of polymer 1, where the reticulation step induces a broadening of the peaks in the range 55-85ppm, a confirmation that the reaction has occurred.

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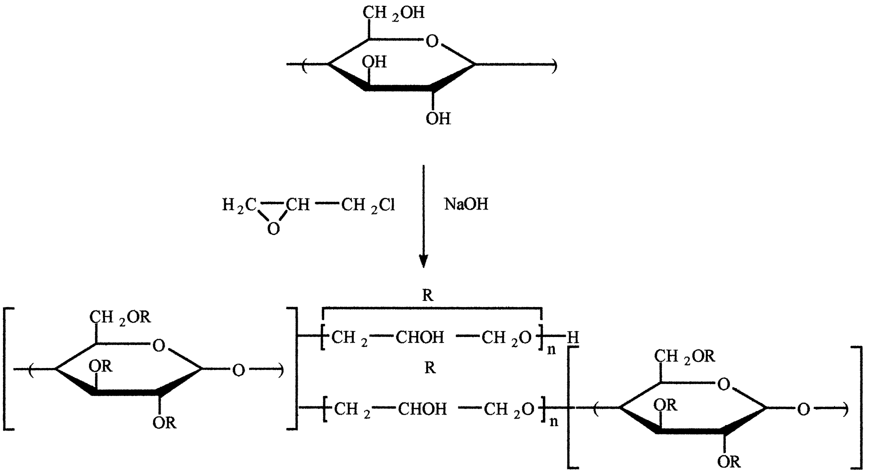
All the polymers give identical CPMAS spectra, suggesting that the signals due to the crosslinking agent are completely hidden by the $C_{2,3,5}$ glucose peaks. Similar results have been already published9). In this paper, we describe also the complexing properties of these polymers toward organic pollutants using the batch method. In particular, the influence of several kinetics parameters on the sorption capacity is evaluated and discussed.



Scheme 1. Synthesis of crosslinked starch-polymers.

Results

Fig. 2 shows the sorption capacity of polymer 5 versus stirring time toward the three chlorophenol isomers. One hour was sufficient for reaching the maximum capacity. The order of the adsorption capacity for the pollutants examined is the following: meta-chlorophenol (mClP) > para-chlorophenol (pClP) > ortho-chlorophenol (oClP)3). The quantity of each pollutant adsorbed is significant, and in particular, mClP isomer exhibit high sorption using these systems. These results can be explained by physical and steric adsorption due to the polymer network introduced by the epichlorohydrin, and by the formation of hydrogen bond interactions such as guest-polymer. We suppose that the crosslinking agent plays the most important role in the sorption mechanism.

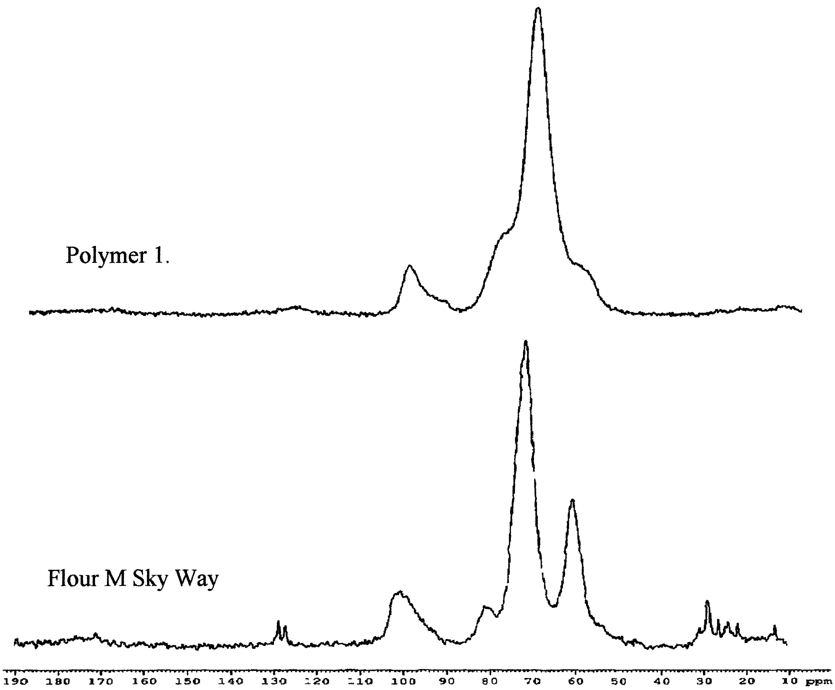


Fig. 1: CPMAS spectra of starch-enriched flour and a crosslinked polymer.

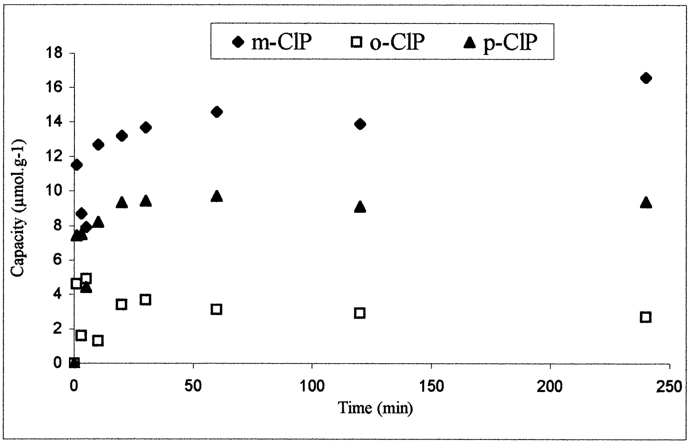


Fig. 2: Kinetics of sorption capacity (in µmol/g) of the three chlorophenol isomers by starch-enriched flour polymer 5 (concentration 5.10^{-4} mole/l).

Fig. 3 shows the sorption capacity of polymer 5 versus the starting concentration of pollutants. The quantity of polymer was kept constant while the molar concentration of the guest molecule was varied. The sorption capacity increases with increasing the starting concentration of the solute. The trend of the curves reflects the affinity of the guest compound for the material. These results can be explained by the fact that not only the crosslinking agent plays an important role in the sorption mechanism, but that other interactions, probably hydrogen bond interactions between the solute and the polymer, and also hydrophobic solute-solute interactions are involved.

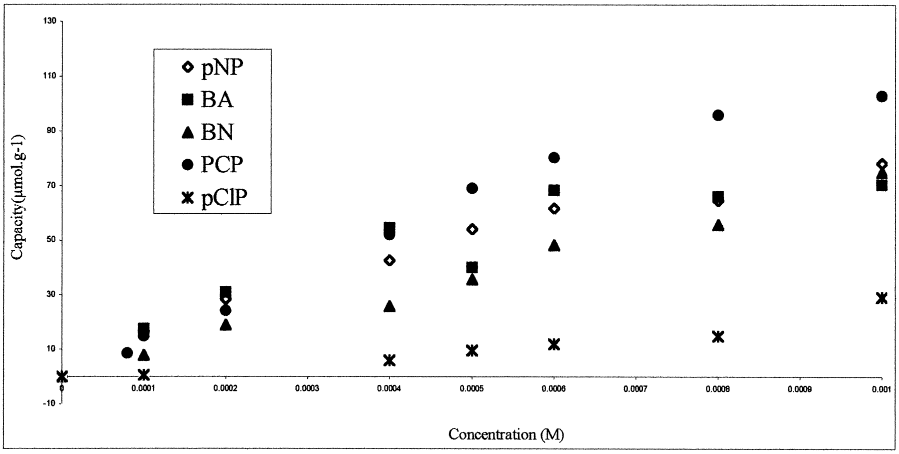


Fig. 3: Influence of the starting concentration on the sorption capacity (in μmol/g) in water (contact time 1h).

Figure 4 shows the influence of the amount of epichlorohydrin on the sorption capacity. For this study, we used four polymers prepared using different amounts of epichlorohydrin. These results show that the sorption capacity increase with the increase of the amount of epichlorohydrin and are highly influenced by this parameter. They confirm that the crosslinking agent creates a network structure in the polymer chain which induce a steric effect (physical adsorption). An HRMAS experiment, and also the determination of relaxation parameter are in progress to confirm a more extensive reticulation for the polymer of high amount of epichlorohydrin, and thus, the important role of the physical adsorption.

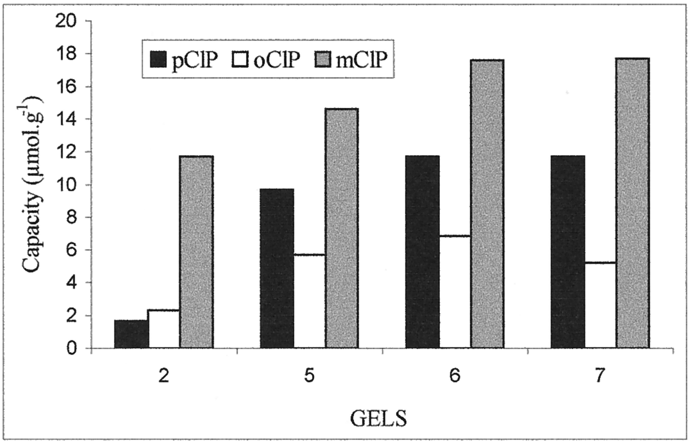


Fig. 4: Influence of the amount of epichlorohydrin on the sorption capacity (in µmol/g) of the three chlorophenol isomers (concentration 5 10^{-4} mole/l).

Conclusion

Adsorbents made from insoluble crosslinked starch-polymers possess specific inclusion recognition capabilities with phenolic compounds. The results indicate that these materials are high capacity adsorbents. The mechanism of sorption is both physical adsorption in the polymer network and/or the formation of hydrogen bond and hydrophobic interactions such as guest-polymer and guest-guest interactions.

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