PREFACE

Interrelation between the structure and adsorption properties in respect to water and nitrogen vapors and Ni, Cu and Ag cations from solutions by modified chitosan samples is studied. IR spectroscopy, X-ray diffraction and pulsed NMR experiments show the influence of the preliminary treatments as freeze-drying after precipitation with NaOH or Na_2CO_3 or drying in air, as well as cross-linking on the supramolecular structure. The more ordered structure is observed in the freeze-dried samples of chitosan compared with the air-dried sample. The parameters of porous structure of the chitosan samples calculated from the isotherms of water vapors adsorption at 293 K and the nitrogen vapors adsorption at 77 K are compared. It is revealed that the isotherms of water vapors adsorption on the chitosan samples are more sensitive to the structural modification of polymers. The efficiency of different models based on the Flory-Huggins, Dubinin-Astakhov, and Dubinin-Serpinsky equations for fitting the experimental isotherms of water vapor adsorption is evaluated. The Dubinin-Serpinsky equation 2 based on a model of two-stage localized adsorption of water molecules describes the experimental water vapor adsorption on the chitosan samples in the full range of relative pressures. In the range of small relative pressures, water molecules interact with chitosan polar groups which serve as the primary adsorption centers (PAC). Then, water molecules adsorbed on PAC become the secondary adsorption centers for further adsorption. As a result, at relatively high pressures the water clusters are formed. In the range of low water fillings of the chitosan adsorbents, the amount of primary adsorption centers can be evaluated by the comparative method.

The freeze-dried chitosan samples display the increased adsorption capacity in respect of water and nitrogen vapors, as well as to metals cations.

The cross-linking of the freeze-dried chitosan samples by glutaraldehyde reduces the adsorption capacity through the blockage of amino-groups. Cross-linking the chitosan films leads to the growth of adsorption capacities towards to water vapors. Thus, the analysis of the isotherms of water vapors adsorption specifies that structural changes of the chitosan samples after freeze drying and cross-linking resulting in a growth of the amount of accessible adsorption centers.

The adsorption capacities and the rates of adsorption of metal cations as Ni, Cu and Ag onto the modified chitosan samples are examined. The Langmuir, Freundlich and Dubinin-Radushkevich adsorption models are used to describe the isotherms of metal cations adsorption. The kinetics experimental data properly correlate with the pseudo-first-order kinetic model. The modification of the chitosan structure by freeze-drying noticeably increases the adsorption of metal cations. The adsorption capacity of the freeze-dried chitosan sample in respect of nickel cations is as high as 4.5 mmol/g that is threefold higher than that of the air-dried chitosan sample.

The IR-VIS spectroscopic experiments performed for the copper cations adsorption on the chitosan samples at high adsorption values allowed to advance a probable model of copper-chitosan complex that is a "bridge" structure based on a binuclear copper complex which bounds two chitosan macromolecules, so that every Cu (II) cation of a pair is associated with one amino group in axial position which belongs to different chitosan chains.