Structure, morphology and sorption properties of lignin ion-exchangers

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Novel nano-, micro- and macroporous ion-exchangers have been synthesized by chemical modification of lignin with epoxy-diane resin ED-20 and oligomer of epichlorohydrin with subsequent amination of intermediate glycidyl and chlorine derivatives. Influence of nature and ratio of interacting compounds, temperature and duration of modification on stricture, phase composition, morphology and physical chemical, sorption properties of sorbents have been studied by FTIR, high resolution SEM and TEM, XRD, DSC, DLS and porosimetry methods.

XRD results testify to the presence of amorphous (80%) and crystal (20%) phases in initial lignin polymer. Identification of crystal component has shown the presence of cellulose. As hardly hydrolyzed polysaccharide it has strong chemical bonds with lignin cellular wall and it remains in vegetative tissue after acid hydrolysis. Calculated roentgenograms show high and low intensive reflexes corresponded to cellulose at 2θ=34-51° and 2θ=14-23° respectively. Decomposition of the narrowest and intensive peak (002) at 22,53° by Lorentz's functions allows to identify three types of cellulose structure: crystal linear, crystal deformed (bent) and amorphous.

It is established that epoxidation and amination of lignin lead to decrease of crystallinity index of modified polymers (13-15%) in comparison with untreated sample (20%). It is apparently connected with decreasing of amount of cellulose crystal component and increasing of content of amorphous phase. Increase of molecular weight of polyamines also leads to decrease of crystallinity index of final products. It was found that isothermal annealing of samples at 135°C for 1-7 hours results to gradual increase of crystallinity index of initial polymer (23-28%) and products of its epoxidation (20-24%). The increasing of amount of crystal phase at heating is probably caused by growth of amount of oriented cellulose macromolecules due to their ordering.

SEM and TEM images of sorbents testify to presence of isolated spherical, slit-like, tubular pores and their combinations ranging from several nanometers to tens of microns. Modification leads to decrease of S_{BET} of ion-exchangers (9,2-5,2 m^2/g) in comparison with initial polymer (14,5 m^2/g) due to incorporation of epoxy and amine compounds into lignin inner and outer surface. Low size of S_{BET} of lignin and ion-exchangers indicates on their macroporous structure. Mesopore size distribution curves show that ion-exchangers mainly contain mesopores with diameter 10-14 nm.

Synthesized ion-exchangers were used for sorption of toxic metabolites from blood serum of diabetic retinopathy patients and laboratory rats with diabetes and pancreatitis. In vitro tests show that lignin ion-exchangers are capable to selective extract triglycerides, atherogenous fractions of cholesterol (LDL-C, VLDL-C), bilirubin, glucose, creatinine, urea and digestive enzymes – trypsin, lipase, alkaline phosphatase and also aminotransferase and aspartate aminotransferase from biological fluids without destroying of their proteinaceous and electrolytic composition. As a result of effective removal of carbohydrates, lipids and ferments their content reduced from pathological to the optimum compensated level or physiological norm. Due to these fine detoxication properties lignin ion-exchangers can be used as enterosorbents for correction of metabolic violations and decreasing risk of diabetes and pancreatitis.