Synthesis and Application of Nano-, Meso- and Macroporous Sorbents Based on Lignin for Detoxication of Biological Fluids

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Abstract. Novel nano-, meso- and macroporous sorbents based on hydrolysis lignin have been synthesized by catalytic *o*-alkylation of biolpolymer with epoxy resin ED-20 and subsequent amination of formed α-oxyde derivative. Composition, structure, morphology and physical, chemical properties of ion-exchangers were investigated by FTIR, SEM, TEM, porosimetry and potentiometric titration method. It has been established that alkaline activated lignin shows an increase of S_{BET} to 20.9 m^2/g while modification leads to decrease of S_{BET} more than double (from 9.2 to 5.2 m^2/g) that of an untreared sample (14.5 m^2/g). Synthesized sorbents are characterized by approximately identical mesoporous structure and mainly contained a pore size of 10-14 nm. The results clearly demonstrate the efficiency of lignin based sorbents for the removal of water and lipid soluble toxic metabolites from blood serum of diabetic retinopathy patients. Samples reduced the high level of total cholesterol, including its most atherogenic fractions (LDL-C, VLDL-C), triglyceride to the level of optimum compensated diabetes without significant removal of HDL-C. Concentration of glucose was decreased to physiological norms.

Keywords: nano-, meso- and macroporous sorbents, lignin, cholesterol, glucose, lipoproteids, sorption, detoxication.

INTRODUCTION

Lignins are natural polymers exhibit promising capacities as pollutant adsorbents. They have been investigated in recent years as sorbents due to low-cost, availability, biodegradability and renewability [1-10]. In contrast with such raw materials as oil, coal and gas that permanently decrease because of continuous consumption. Some previous studies and report the use of lignins for quantitative removal of heavy metals ions [1-5] and various organic compounds including pesticides [6], dyes [7,8], traces of phenol from waste waters of phenol formaldehyde resins production [9], bile acids, cholesterol and other metabolites from biological fluids [10]. Lignins accumulate these pollutants due to their fine porous structure and a set of different functional sorption active groups such as hydroxyl, carboxyl, carbonyl and ether groups. The presence of different oxygen-containing groups in their matrix is prerequisites for pollutant extraction by physical adsorption, covalent or hydrogen bonding, coordination or ion-exchange interactions.

The relatively low solubility and toxicity of hydrolysis lignin, which has cross-linked structure, in contrast to other commercial lignins (water-soluble lignosulphonates and alkali-soluble kraft lignin) allow using it in medicine and veterinary as an effective hemo- and enterosorbents for purification of biological fluids from pathogenic substances [12-14]. It exhibits the high sorption ability to bacterial cells and toxins produced by them, lipids and water soluble methabolites. Hydrolysis lignin also possesses better extracting properties than activated carbon, chitin and chitosan in relation to creatinine, urea, ammonia, xenobiotics, heavy metals, radioactive isotopes, allergens, microbes. It promotes their accelerated removing from an organism. Due to these properties lignin is allowed for prevention and treatment of different diseases of human and animals (cholecystitis, dysbacteriosis, salmonellosis, dysentery, peritonitis, poisonings, allergies and etc.) [12,13].

Further activation and functionalization of this biopolymer by chemical modification lead to increase of sorption capacity and selectivity to toxins. Besides incorporation of functionally active compounds into lignin change of its textural properties in particular, enhanced of mesoporosity, which significantly increases the adsorption properties compared to untreated raw material [3-5, 8,10,11].

The aim of the present study is development and use of a new nano-, meso- and macroporous sorbents based on hydrolysis lignin of cotton husk for detoxication of blood serum of diabetic retinopathy patients.

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Preparation and Characterization of Nano-, Meso- and Macroporous Sorbents Based on Lignin

The nano-, meso- and macroporous anion-exchangers were synthesized by *o*-alkylation of lignin with epoxy resin ED-20 in the presence of triethylamine (TEA) catalyst and subsequent amination of α-oxide derivative of lignin (Lignin-ED-20) with polyethyleneimine (PEI), polyethylenepolyamine (PEPA) and 2-vinylpyridine (2-VP). Conditions of synthesis of Lignin-ED-20 are shown in table 1.

TABLE 1. Influence of catalyst concentration on characteristics of α-oxide derivative of lignin (t=100ºC, τ=1h).

[ED-20] : [TEA], mol.	Element Composition C	Element Composition H	Epoxyde Group Content, %	Weight Gain, %	Swelling Degree, %
1.0 : 0.0	56.10	6.47	0.0	0.00	53.7
1.0 : 0.5	60.26	7.10	4.05	20.53	102.0
1.0 : 1.0	63.50	7.20	4.65	26.10	114.3
1.0 : 2.0	62.92	7.19	4.20	25.20	99.5
1.0 : 5.0	60.66	7.09	2.20	21.40	58.8

As shown in table 1 the content of α-oxide groups in the Lignin-ED-20 increased with the increasing molar fraction of catalyst. The amount of α-oxide groups reached maximum at the equimolar ratio of ED-20 to TEA. Further increasing the TEA concentration did not increase the epoxide content, weight gain, carbon content or swelling degree of semiproduct. This is due to extensive proceeding of side reactions of ED-20 in the presence of a large amount of amine leading to di-, trimerization and polymerization of epoxide resin.

To prepare ion-exchangers modified lignin with 4.65% of α-oxide groups was aminated with PEI, PEPA and 2-VP. Influence of a ratio of reacting components, temperature and duration of amination on characteristics of synthesized ion-exchangers has been investigated. It is established that the static exchange capacity (SEC) of the sorbents increases regularly with increasing content of aminating agent in the reaction mixture. The optimal conditions of synthesis and the characteristics of sorbents based on lignin are shown in table 2. Further increasing of the amount of amines does not lead to increase of SEC, but causes the formation of polyelectrolytes with low yield, high specific volume (V_{spec}) and low mechanical strength. The pK of active groups of sorbents based on aliphatic polyamines show that their belong to weak-based anion-exchangers and contain primary, secondary and tertiary aliphatic amine groups. Sorbent containing heterocyclic amine 2-VP belongs to highly basic ion-exchanger.

TABLE 2. The optimal conditions of preparation and characteristics of ion-exchangers based on lignin.

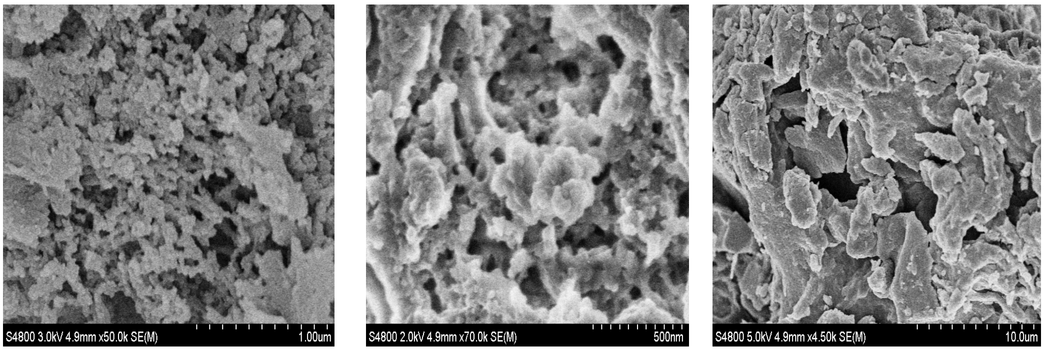
Sorbents	Optimal Conditions [Lignin-ED-20] : [Amine], Mass. Part	T, ºC	T, h	SEC, mequ/q, HCI	SEC, mequ/q, NaCI	N, %	Yield, %	V_{spec}, ml/g	pK
Lignin-PEI	1.0 : 1.5	40	2	3.00	0.38	12.84	99.90	7.56	6.76
Lignin-PEPA	1.0 : 0.75	40	1	2.15	0.22	8.91	90.13	3.87	6.20
Lignin-2-VP	1.0 : 1.0	60	1	-	1.24	6.64	92.31	3.20	2.50

Adsorption characteristics of lignin and sorbents were investigated by method of nitrogen vapor adsorption using BET model. Low size of a specific surface area (S_{BET}) and high total pore volume (ΣV_{pore}) of sorbents indicate about macroporous structure of samples (Table 3). The results show that activation of lignin with 1.5% NaOH at 60ºC leads to increase of S_{BET} in comparison with an extracted sample. But modification decreases its surface area, probably, due to filling of cavities and channels of biopolymer with epoxy and amine compounds.

TABLE 3. Adsorption characteristics of lignin and sorbents.

Sample	Extracted Lignin	Activated Lignin	Lignin-PEI	Lignin-PEPA	Lignin-2-VP
S_{BET}, m^2/g	14.5	20.9	5.2	9.2	6.5
ΣV_{pore}, mL/g	0.14	0.16	0.13	0.12	0.08

SEM and TEM images of sorbents testify that the surface of cell-wall tissue is not fully covered by layer of modifying polymers (Figures 1,2). The superficially modified lignins reasonably save the porous structure of initial polymer. Images indicate the presence of large macroporous of varying diameter from 50 to 700 nm, mesoporous from 2 to 50 nm and nanoporous nearly 0.8 – 1.8 nm. According to size distribution curves presented in Figure 3, synthesized ion-exchangers are characterized by approximately identical mesoporous structure and mainly contain mesoporous with diameter 10-14 nm.



(a) **(b)** **(c)**

FIGURE 1. SEM images of nano-, meso- and macroporous sorbents based on lignin, modified by PEI (a), PEPA (b) and 2VP (c).

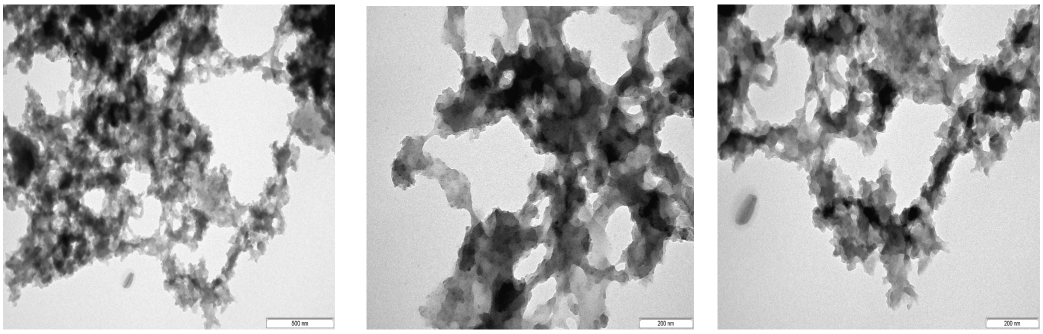


FIGURE 2.TEM images of nano-, meso- and macroporous sorbents based on lignin, modified by PEI (a), PEPA (b) and 2VP (c).

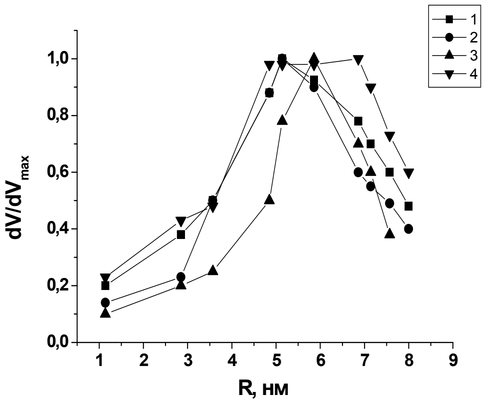


FIGURE 3. Pore size distribution curves of lignin (1) and sorbents with groups of PEI (2), PEPA (3) and 2-VP (4)

In particular pH resistant and mechanical durable nano-, meso- and macroporous sorbents with amine ligands, grafting on lignin are used for removal of water- and lipidsoluble pathogenic components from blood serum of diabetic retinopathy patients.

Purification of Blood Serum of Diabetic Retinopathy Patients Using Lignin Based Sorbents

Blood serum of ophthalmologic patients is typically characterized by carbohydrate-lipid risk factors. These are a high level of total cholesterol and its atherogenic fractions such as LDL-C, VLDL-C, triglyceride (TG), glucose and low content of HDL-C. Average concentration of these metabolites in analyzed serum exceeded physiological normal values by factors of 1.67, 2.02, 4.60, 2.09 and 1.23 respectively. Content of HDL-C was below more than twice. Biochemical indicators of blood serum before and after contact with sorbents are shown in Figure 4.

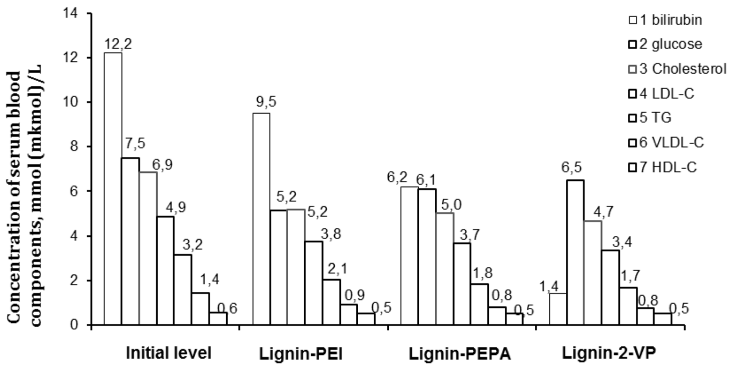


FIGURE 4. Detoxication of serum blood of diabetic retinopathy patients.

After contact with sorbents the total cholesterol level and average concentration of LDL-C, VLDL-C decreased to the level of optimum compensated diabetes (<4.8–6.0 mmol/L, <3.0–4.0 mmol/L respectively). The degree of HDL-C extraction insignificantly decreased from 0.68 to 0.50 mmol/L. Purification of serum blood proceeded not only by removal of atherogenic fractions of cholesterol, but also by adsorption of large amounts of TG, bilirubin and glucose. After sorption concentration of TG decreased from 3.14 mmol/L to 2.1–1.71 mmol/L that corresponds to level of optimum compensated diabetes (<1.7–2.2 mmol/L). The most indicative criteria of biological liquid detoxification from lipid substances is cholesteric index of atherogenicity. Its value is significantly decreased from 10.81 to 8.33 after contact of serum with samples. This is caused by the high adsorption degree of atherogenic fractions of cholesterol and a very low degree of HDL-C removal. As a result of effective uptake of glucose its content decreased from pathological levels (7.50 mmol/L) to 5.2 – 6.1 mmol/L that corresponds to physiological norm (< 4.2 – 6.1 mmol/L).

Considerable hypolipidemic and hypoglycemic effects of nano-, meso- and macroporous sorbents based on hydrolysis lignin have potential application in medicine, biology and biotechnology as immune-stimulating and organ-protection agents. They can be used as hemo-, enterosorbents for detoxification of biological fluids and the treatment of diabetes, decreasing risks of diabetic retinopathy and normalization of the carbohydratelipid status of organisms.

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