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New Technology for the Synthesis of New Materials Based on Cellulose and Sorption of Noble Metals

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1. Introduction

Cellulose is continuously updated biopolymer through photosynthesis and, hence, it is inexhaustible raw material for new materials and new technology (Bojanic et al., 1988a; Granja et al., 2006; Hubbe et al., 2008, 2011; Jovanovic et al., 2002; Kamel, 2007; Puoci et al., 2008; Schwanninger et al., 2004; Vainio, 2007; Wu et al., 2007; Zhang et al., 2010). Modification of biopolymers has been given scientific and practical importance. Grafting is one of the best methods making the synthesis of new materials and their applications virtually unlimited (Achilleos & Vamvakaki, 2010; Bhattacharya & Mirsa, 2004; Cohen Stuart et al., 2010; Crini, 2005; Gandini, 2008; Li et al., 2011; Lu et al., 2008; Roy et al., 2009; Petrovic et al., 2010; Sharma et al., 2010; Xin et al., 2011). Cellulose is, due to its chemical and sub-molecular structure, mechanically resistant and chemically stable. Such properties are of great importance for the chemical and electrochemical modification and represent a subject to numerous studies aimed at obtaining new materials with special properties for specific applications (Anderson, 2000; Bonne, 2008; Chmielewska et al., 2010; Cao et al., 2007; Hu et al., 2009; Kim et al., 2010; Pinto & Maaroufi, 2005; Spiridon et al., 2011; Vitz et al., 2010; Wang, 2008; Zhou et al., 2011). Grafting reactions represent possible solutions for changing chemical, physical and mechanical properties of the cellulose molecules in desired direction. Modification of cellulose leads to formation of the new ionic polymers (Heinze, 1998) and grafting of N-vinyl pyrrolidone (Gupta & Sahoo, 2001; Chauhan et al., 2005), styrene, methyl methacrylate, methyl acrylamide (Coshun & Temuz, 2005; Sharma & Chauhan, 2009) acrylamide and acrylic acid (Chauhan & Lal, 2003), grafting of acrylamide (Chauhan et al., 2003) and 4-vinylpyridine (Chauhan et al., 2000; Kaur & Dhiman, 2011), and ethyl acrylate (Kalia et al., 2011) on cellulose have been studied. New materials based on biopolymers and, especially, modification of cellulose and lignin, have been used as semipermeable membranes, ion-exchangers and matrices for medicaments (Bilba, 1998; Hubicki et al., 2008; Maliyekkal et al., 2010; Nada et al., 2007; Ozdemir et al., 2006; Parajuli, 2006; Rodriguez et al., 2009; Saarinen, 2008; Vlasankova & Sommer, 1999; Wang, 2005; Xu, 2005). In order to obtain grafted cellulose copolymers with 4-vinylpyridine, vinylimidazole, 1-vinyl-2-pyrrolidone, 9-vinylkarbazole and other vinyl monomers containing double bonds capable for copolymerization with vinyl monomers have been introduced in cellulose. For

the induction of double bonds in cellulose, the reaction with acyloyl chloride from which cellulose acrylate has been produced under equal concentrations of reactants and an equal reaction time under procedure described by (Akelah & Sherrington, 1981) is used. They have synthesized acrylate cellulose with degree of substitution, DS = 0,81 where on C_6 – polysaccharide unit in average came 0.81 of acrylic residue with grafted styrene on it, but without consideration of the optimization of cellulose acrylate synthesis. The procedure for the synthesis of cellulose acrylate has changed itself. Its optimization was done and a new molar ratio of reactants was given in reaction mixture with different reaction times. Grafting reaction was conducted by radical polymerization of 4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pirrolidone and 9-vinylcarbazole. Grafed copolymers were synthesized (new materials): cellulose-poly-4-vinylpyridine, cellulose-poly-1-vinylimidazole, cellulose-poly-1-vinyl-2-pyrrolidine and cellulose-poly-9-vinylcarbazole. Quaternization of pyridine ring was performed on grafted cellulose copolymers: cellulose-poly-4-vinylpyridine and cellulose-poly-1-vinylimidazole with methyl iodide. New materials based on cellulose in ionic form at constant potential were synthesized by electrolysis. Electrochemical modification was performed on new cellulose materials with different ions originating from the used basic electrolytes. Thermal and ion-exchanger properties were determined on synthesized new cellulose based materials and they were used as selective ion-exchaners for extraction of noble metals from aqueous solutions. Optimization of the cellulose acrylate synthesis process was used as a model for the synthesis of grafted copolymers of lignin and tannin.

2. Optimization of cellulose acrylate synthesis process and grafting of 4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pyrrolidone, and 9-vinylcorbazole

This experiment was performed with a sample of powdered microcrystalline cellulose form Aldrich company. Before using the cellulose, powder was subsequently rinsed with water, ethanol, methanol and acetone, and then dried at 50°C. Parameters important for optimization of the synthesis of cellulose acrylate and that were considered were: molar ratio of reactants in reaction mixture of cellulose/potassium-t-butoxide/acryloyl chloride = 1:3:10, and different synthesis reaction times of cellulose acrylate of 1,3,5,8 and 10 hours. Cellulose acrylate and grafted cellulose copolymers with 4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pyrrolidone and 9-vinylkarbazole were synthesized according the methods and procedures described by (Bojanic, 1994, 2010). Cellulose acrylate (Cell-acrylate) was synthesized by making 3.24 g-0,02 mol of cellulose swell in 50 ml of acetonitrile for one hour at room temperature. Potassium-t-butoxide 6.72 g-0.06 mol was dissolved with mild heating in 50 ml of acetonitrile and the reaction with the cellulose solution at room temperature, with mixing, during 4 hours took place. Formed potassium-cellulosate was not isolated, and overplus of acryloyl chloride was added in it, namely 18g-0.2 mol in 50 ml of acetonitrile at 25^0C. Reaction mixture was mixed and refluxed during 10 hours. Cellulose acrylate was then washed with water, ethanol, methanol and acetone and dried at 50^0C. 4.65 g of product was obtained which has a band at 1720 cm^{-1} from ester carbonyls in IR-spectrum in KBr. Elemental analysis of samples taken after 1, 3, 5, 8, 10 hours provides optimum time of 10 hours. During this period, the reaction gave a product with a degree of substitution (DS) of 2.4. The same procedure was repeated for lignin and tannin, with the difference that instead of cellulose the same weight amount of lignin and tannin was taken. The only difference is that the tannin acrylate was not elutriated with water because it is being dissolved in it. The resulting tannine acrylate and lignin acrylate have characteristic band at 1720 cm^{-1} in the IR-

spectrum. Synthesis of cellulose poly-4-vinylpyridine (PVP-Cell) was performed as follows: Grafting of 4-vinylpyridine on cellulose acrylate was done by adding 1 g-0.0046 mol of acrylate cellulose, 5ml-4,88g-0,046 mol of 4-vinylpyridine and 0.05 g azobisisobutyronitrile (AIBN) in 50 ml of acetonitrile. Reaction mixture was mixed and refluxed for 5 hours in a stream of nitrogen. 1,1g of Cell-PVP was obtained, and it was characterized by IR spectroscopy with characteristic IR-spectrum bands at 1620, 990 and 820 cm^{-1}. Sorption of gold after 1 and 24 hours was 98.12 and 99.63 wt.%. The capacity was 0.2 g Au/g ion-exchanger. In comparison, the capacity for Pd and Pt is about 0.03 g/g ion-exchanger.

Synthesis of lignin poly-4-vinylpyridine (Lig-PVP) was performed as follows: the procedure was the same as for the synthesis of Cell-PVP, but instead of cellulose, 1g of lignin was taken. 1,1g Lig-PVP was obtained, and it was characterized by IR spectroscopy with characteristic IR-spectrum bands at 1620, 990 and 820 cm^{-1}. Obtained Lig-PVP does not swell in water. However, in a solution containing Au, Pd and Pt ions, it swelled 100 wt%. Sorption of Au was fast and complete and the capacity was 0.211 g Au/g ion-exchanger. This capacity was confirmed in the strong acidic electrolytes in which both Pt and Pd are present. Regeneration with HCl (1:1) was complete. By checking the capacity with 0.1 M solution of Au it was noticed that the yield was 0.4 g Au/g ion-exchanger. The sorption of platinum metals was studied as well, and it was very good.

Synthesis of tannine poly-4-vinylpyridine (Tan-PVP) was performed as follows: the procedure was the same as for the synthesis of Cell-PVP, but instead of cellulose, 1g of tannine was taken. 1.1g of Tan-PVP was obtained, and it was characterized by IR spectroscopy with characteristic IR-spectrum bands at 1620, 990 and 820 cm^{-1}. Sorption of Au for Tan-PVP has not been tested because it is soluble in water.

Synthesis of cellulose poly-1-vinylimidazole (Cell-PVIm) was performed as follows: The procedure for the synthesis of Cell-PVP was repeated and grafting of 1-vinylimidazole 4 ml-0.044 mol on cellulose was performed. Cell-PVIm, 1.1g was obtained. Cell-PVIm was characterized in the IR-spectrum with characteristic bands at 1620, 1480, 910, 820 and 740 cm^{-1}. It did not swell in water and the sorption of gold was 0.23 g Au/g ion-exchanger. Synthesis of cellulose-poly-1-vinyl-2-pyrrolidone (Cell-P1V2P) followed the procedure for the synthesis of Cell-PVP and grafting of 1-vinyl-2-pyrrolidone, 5 ml - 0.047 mol, was performed afterwards. Cell-P1V2P, 1.1g was obtained with characteristic IR-spectrum bands at 1650, 1310 and 890 cm^{-1}. Copolymer blured by swelling and it changed color into brown-red. Sorption of Au after 1 and 24 hours was 25.50 and 54.08 wt.%. The capacity of Au was 0.20 g Au/g ion-exchanger. Synthesis of cellulose-poly-9-vinylcarbazole (Cell-P9VK) followed the procedure for the synthesis of Cell-PVP and grafting of 9-vinylcarbazole, 5g-0,047 mol, on cellulose was performed afterwards. 1.2 g of copolymer was obtained with characteristic IR-spectrum bands at 1580, 1310, 1210, 740 and 720 cm^{-1}. Sorption capacity of Au has not been tested. Synthesis of cellulose 1-methyl-poly-4-vinylpyridine iodide (Cell-1-Me-4-PVPJ) was derived as follows: Cell-PVP, 2g-0.0043 mol was mixed with 5ml-11.4 g-0.08 mol of methyl-iodide in 50 ml of dimethylformamide (DMF) and it was refluxed with constant mixing for 5 hours. The reaction produced 2.1 g of Cell-1-Me-PVPJ which was filtered and rinsed with water, acetone, ethanol and methanol, and finally dried at 50^{0}C. Elemental analysis of Cell-1-Me-PVPJ was in good accordance with the theoretically calculated values. Sorption of Au after 1 and 24 hours was 99.03 wt.% and 99.89 wt.%. The capacity of Au was 0.24 g Au/g ion-exchanger. In contact with the Au

solution, Cell-1-Me-PVPJ changed color into brown-red, which concludes the creation of a gold nanoparticles (Srivastava et al., 2008). Synthesis of lignin 1-metylpoly-4-vinylpyridine iodide (Lig-1-Me-PVPJ) and tannin 1-metylpoli-4-vinylpyridine iodide (Tan-1-Me-PVPJ) was performed in the same manner as the synthesis of Cell-1-Me-PVPJ with the difference that Lig-PVP and Tan-PVP with methyl iodide was used. Sorption of Au of the new obtained materials has not been tested. Synthesis of Cellulose 3-metylpoly-1-vinylimidazole iodide (Cell-3-Me-PVImJ) was performed the same as synthesis of Cell-1-Me-PVPJ, with difference that Cell-PVIm with methyl iodide was used. Cell-1-Me-3-PVImJ blured by swelling in contact with Au solution and it changed color into brown-red. The capacity of 0.20 g Au/g ion-exchanger was reached. The degree of polymerization of microcrystalline cellulose was determined by viscometer in cupriethylenediamine as solvent at 25°C, and elemental analysis was performed with the Perkin-Elmer instrument, model 240. IR-spectra of the initial cellulose and obtained copolymers were determined by Perkin Elmer spectrophotometer, model IRDMI-FTIR1724X, using KBr technique. Optimization of the synthesis process of cellulose acrylate was carried out by a series of experiments in which the impact of the relation between reactants in reaction mixture and reaction time on the cellulose acrylate has been examined, i.e. the degree of substitution (Bojanić, 2010). In the IR-spectrum, very pronounced band at 1720 cm^{-1} was observed, which corresponds to C = O group from esters.

Table 1. shows the dependence of content (C,%; H,%; O,%) from the reaction time, compared to the components in the reaction mixture (cellulose/potassium-t-butoxide/acryloyl chloride = 1:3:10). Samples for elementary analysis were taken after 1, 3, 5, 8 and 10 hours of reaction. It is evident from Table 1. that the content of C (%) in cellulose acrylate increases with increase in reaction time.

Microanalysis	% C	% H	% O
$C_9H_{12}O_6$	50.00	5.60	44.40
$C_9H_{12}O_6$ -1h	44.00	6.18	49.82
$C_9H_{12}O_6$ -3h	45.02	6.16	48.82
$C_9H_{12}O_6$- 5h	45.65	6.08	48.27
$C_9H_{12}O_6$- 8 h	46.50	6.03	47.47
$C_9H_{12}O_6$-10h	47.02	5.97	47.01

Table 1. Elemental analysis: C, H and O content in molar ratio cellulose/potasium-t-butoxide/acryloy chloride of 1:3:10 after various reaction times.

The percentage of subtitution of glucose units in cellulose (Y) is calculated according to equation (1) based on the results of elemental analysis:

$$Y = (A-B)/(C-D) \times 100 \qquad (1)$$

a.   % C specified in the grafted cellulose copolymer,
b.   % C determined in the initial cellulose,
c.   % C calculated at 100% derivatisation,
d.   % C from the initial cellulose.

Extension of the reaction time increases the content of %C in acrylate as well as %Y, which, for the molar ratio of cellulose/potassium-t-butoxide/acryloyl chloride of 1:3:10 and

New Technology for the Synthesis of New
Materials Based on Cellulose and Sorption of Noble Metals
183

reaction time of 10 hours, is Y=80.7%. The degree of substitution of cellulose acrylate (DS) is calculated from IR spectra using the relations of characteristic bands in equation (2):

$$DS=D_{1720}/D_{1410} \tag{2}$$

DS for cellulose acrylate obtained under optimal synthesis conditions is 2.4 and it is about three times higher than stated by other authors, where DS=0.81 and Y=27% (Akelah & Sherrington, 1981). The optimum conditions for cellulose acrylate synthesis are: molar ratio of cellulose/potassium- t-butoxide/acryloyl chloride = 1:3:10, with the reaction time of 10 hours, and they give DS=2.4 and Y = 80,7%. Fig.1 shows the synthesis of cellulose acrylate and grafting with vinyl monomers. Cell-acrylate (3) is copolymerised with 4-vinylpyridine (4), 1-vinylimidazole (5), 9-vinylcarbazole (6) and 1-vinyl-2-pyrrolidone (7), using AIBN as the initiator of the copolymerization. In the reaction between cellulose acrylate and 4-vynilpyridine Cell-PVP (8) grafed copolymer is formed and its structure was confirmed by IR-spectrum, with characteristic bands at 1620 and 820 cm-1, characteristical for the pyridine molecule.
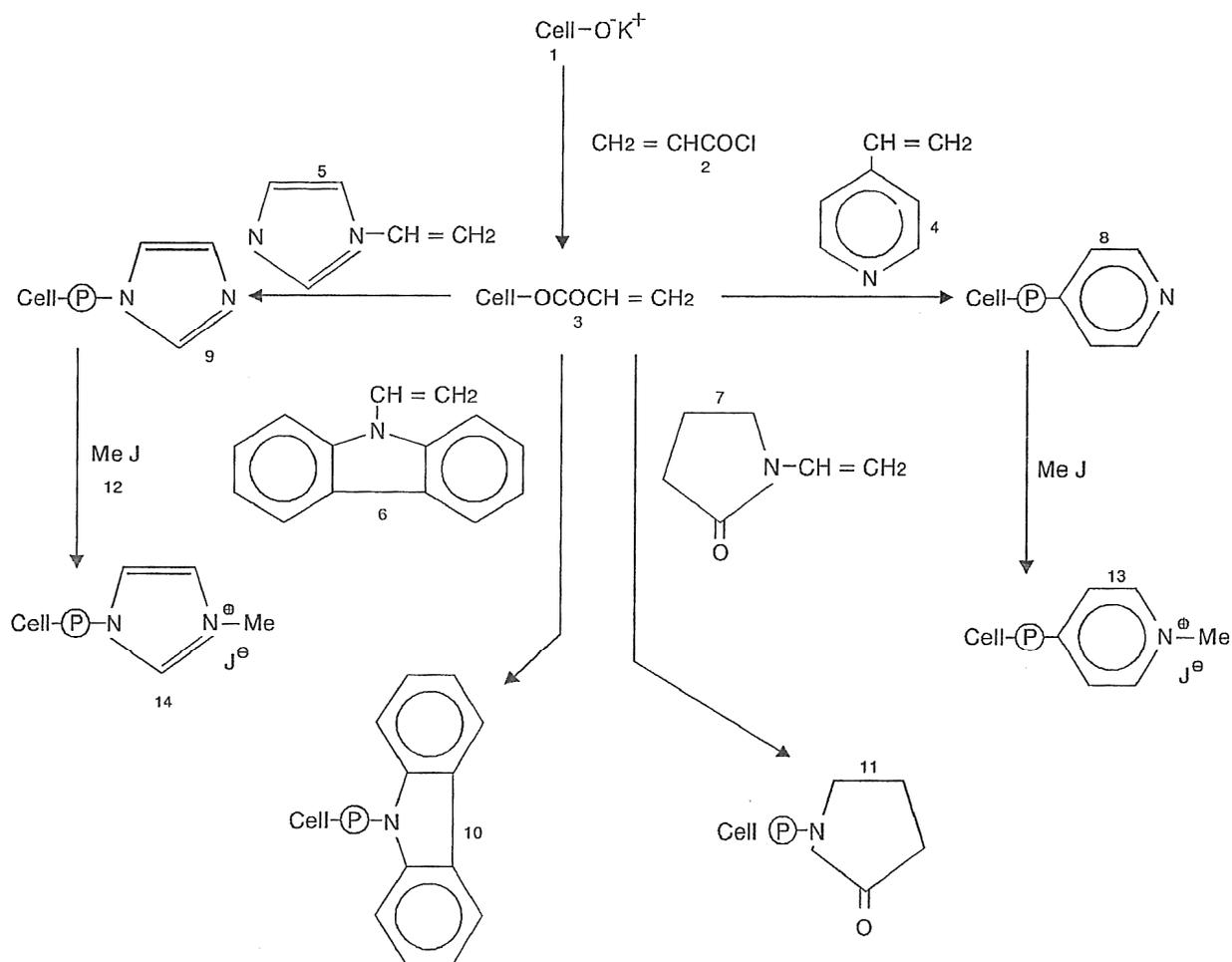

Fig. 1. Cellulose grafted copolymers with vinyl monomers

Reaction between cellulose acrylate and 1-vinylimidazole gives Cell-PVIm (9) and IR-spectrum shows characteristic bands at 1620, 1480, 910, 820, 740 cm-1. Cell-P9VK (10) is formed in reaction between cellulose acrylate and 9-vinylcarbazole, and its IR-spectrum

shows characteristic bands at 1580, 1310,1210, 740, 720 cm⁻¹. Reaction between cellulose acrylate and 1-vinyl-2-pyrrolidone gives Cell-P1V2P (11) and its IR-spectrum shows characteristic bands at 1650, 1310, 890 cm⁻¹. The reaction between Cell-PVP and methyl iodide produces Cell-1-Me-PVPJ (13), while Cell-PVPIm and methyl iodide produce Cell-3-Me-PVIm (14).

The results of elemental analysis of synthesized grafted cellulose copolymers are shown in Table2. In addition to the experimentally determined values, theoretical values for the content of carbon, hydrogen, oxygen, nitrogen and iodine in determined materials calculated from the gross formula of basic structural elements, assuming that all three hydroxyl groups in cellulose molecules have been substituted are shown in Table 2.

Materials	Segments units molar mass	Microanalysis				
		C(%)	H(%)	O(%)	N(%)	J(%)
Cellulose	$C_6H_{10}O_5$	44.4	6.2	49.5	-	-(Teor.)
	162	42.53	6.4	51.07	-	-(Exp.)
Cell-akrylate	$C_9H_{12}O_6$	50.00	5.6	44.4	-	-
	216	47.02	5.97	47.01	-	-
Cell-P1V2P	$C_{15}H_{12}O_7N$	55.00	6.42	34.25	4.28	-
	327	49.93	6.28	41.54	2.25	-
Cell-P9VK	$C_{23}H_{23}O_6N$	67.50	5.60	23.50	3.40	-
	409	77.74	5.20	10.42	6.64	-
Cell-PVP	$C_{16}H_{19}O_6N$	59.80	5.90	29.90	4.36	-
	321	52.43	6.05	36.75	4.77	-
Cell-PVIm	$C_{14}H_{18}O_6N_2$	54.19	5.80	30.97	9.00	-
	310	47.90	5.91	40.43	5,76	-
Cell-1Me-PVPJ	$C_{17}H_{22}O_6N_2$	44.06	4.75	20.79	3.00	27.4
	463	45.11	5.31	26.53	2.93	20.12
Cell-3Me-PVImJ	$C_{15}H_{21}O_6N_2J$	39.82	4.64	21.35	6.19	28.00
	452	42.63	5.39	32.61	5.25	14.12

Table 2. Elemental analysis results of synthetized cellulose copolymers

Based on elemental analysis, specific characteristics of a grafted copolymers of cellulose (mass fraction of grafted copolymer (X); relation of derivatized parts/cellulose vinyl group (Z), the degree of grafting, wt%) are calculated and shown in Table 3.

Materials	Weight fraction of copolymers (X)	Ratio derivatives units/Cell,vinyl groups(Z)	Degree of grafting wt.%
Cell-P1V2P	0.16	0.18	17.80
Cell-P9VK	0.76	1.75	91.53
Cell-PVP	0.16	0.20	35.70
Cell-PVIm	0.05	0.06	19.34

Table 3. Some characteristic of grafted cellulose copolymers

Mass fraction of grafted copolymers is calculated from the following equations:

$$E=(1-X)A+64.8X \text{ (Cell-P1V2P)} \qquad (3)$$

$$E=(1-X)A+87.0X \text{ (Cell-P9VK)} \qquad (4)$$

$$E=(1-X)A+80.0X \text{ (Cell-PVP)} \qquad (5)$$

$$E=(1-X)A+63.8X \text{ (Cell-PVIm)} \qquad (6)$$

From the equations: E=%C found in grafted copolymer, 64.8=%C calculated on 1-vinyl-2-pyrrolidone segment, 87.0=%C calculated on 9-vinylcarbazole segment, 80.0=%C calculated on 4-vinylpyridine segment and 63.8=%C calculated on 1-vinylimidazole segment.

Relation of deriving parts/cellulose vinyl group, Z, is calculated from equation:

$$Z=[(X/M\times100)]/[(1-X)/F)\times Y] \qquad (7)$$

where X and Y are calculated as stated before and F is the average molar mass of cellulose segment adjusted for the degree of subtitution.

$$F=(Y\times G)/100 +[(1-Y)/162]/100 \qquad (8)$$

From equation (8): G is theoretical molar mass of glucose derivates, 162 is theoretical molar mass of glucose residue in the cellulose molecular chain, M is theoretical molar mass of grafted monomers.

The degree of grafting of synthesized copolymers was determined according to equation:

$$\text{degree of grafting} = \%N/AT\times M \qquad (9)$$

where %N is mass percentage of nitrogen in grafted copolymer determined by elemental analysis and AT is atomic mass of nitrogen.

Vinyl monomers, 4-vinylpyridine and 1-vinylimidazole, due to present nucleophilic nitrogen are subject to reactions of nucleophilic substitutions. A typical reaction for the 4-vinylpyridine and 1-vinylimidazole is their quaternization with nucleophilic attack on alkyl halides or by protonation. This type of reaction was used for the synthesis of quaternary cellulose polypyridinium and cellulose polyimidazole copolymers. The reaction of Cell-PVP with methyl iodide yielded Cell-1Me-PVPJ and IR-spectrum showed a characteristic band at 1642 cm^{-1}, which corresponds to C=N$^+$- quaternized nitrogen in the pyridine ring. In reaction between Cell-PVIm and methyl iodide Cell-3Me-PVImJ was formed, whose structure was confirmed by IR-spectra with characteristic band at 1642 cm^{-1} for C=N$^+$, quaternized pyridine. To determine the iodine content in grafted copolymers Cell-1Me-PVPJ and Cell-3Me-PVImJ synthetized from Cell-PVP and Cell-PVIm by quaternization of nitrile atoms with methyl iodide coulometric method was applied.

Coulometric measurement at constant potential of second wave (E = 0.7 V) of cyclic voltammogram in a cell with a diaphragm and Pt-net anode (2 x 3 cm) after mixing (60 min) Cell-1Me-PVPJ grafted copolymer in 0.1 M solution of acetonitrile tetramethylammonium perchlorate melt (CH$_3$CN-Et$_4$NCIO$_4$) was performed and current/time curve was recorded. The amount of electricity needed for complete oxidation of iodide ions into iodide was measured by electrical integrator and content of iodide in the synthesized Cell-1-Me-PVPJ sample was calculated to be 20.12 wt.%.

3. Electrochemical properties of grafted copolymers with 4-vinylpyridine and 1-vinylimidazole

Cellulose acrylate and grafted cellulose copolymers with 4-vinylpyridine and 1-vinylimidazole and their electrochemical transformations in various basic electrolytes were performed by the methods and procedures described in works by (Bojanic et al., 1996). Voltammetric measurements were performed in standard electrochemical cell, which consisted of saturated calomel electrode (SCE), platinum auxiliary electrode and polished platinum disc electrode as working electrode. Electrochemical modification of new cellulose materials was performed in electrochemical cell with a diaphram. Platinum net (4×5) cm was used as working electrode, cathode was from nickel and SCE was used as reference electrode. The cell was connected to the instrument Controvit-Tacussel with potentiostat and function generator type HI-TDK DT 2101 and x-z-y Guold recorder 3054 printer. The results of a simple electrochemical synthesis of new grafted cellulose copolymers in ionic form are shown, using electrolysis at constant potential. Electrochemical transformations of Cell-1Me-PVPJ and Cell-3Me-PVImJ into new grafted cellulose copolymers with different ions originating from the used basic electrolytes was carried out. Electrochemical synthesis of Cellulose 1-metylpoli-4-vinylpyridine perchlorate (Cell-1-Me-PVPClO4) was performed in the following manner: 200 mg of Cell-1-Me-PVPJ was oxidized in the anodic area of electrolytic cell with diaphragm using Pt-net anode (4×5) cm, Ni cathode and SCE in which was 0,1 M solution of $CH_3CNEt_4NClO_4$ at E= 0,7V until starting current drops to the residual current value. The resulting Cell-1-Me-PVPClO4 is filtered, washed with water, ethanol, methanol and acetone and dried at 50°C. Electrochemical transformation of the anions on Cell-1-Me-PVPJ was preformed in the same manner as electrochemical synthesis of Cell-1-Me-PVPClO4 and following new cellulose materials are obtained: Cellulose 1-methyl poly-4-vinylpyridine chloride (Cell-1-Me-PVPCl), Cellulose 1-methyl poly-4-vinylpyridine trifluoroacetate (Cell-1-Me-PVPCF3COO), Cellulose 1-methyl poly-4-vinylpyridine nitrate (Cell-1-Me-PVPNO3), Cellulose 1-methyl poly-4-vinylpyridine p-tosylate (Cell-1-Me-PVPp-TsO), Cellulose 1-methyl poly-4-vinylpyridine tetrafluoroborate (Cell-1-Me-PVPBF4) and Cellulose 1-methyl poly-4-vinylpyridine hexafluorophosphate (Cell-1-Me-PVPPF6). Electrochemical transformations on Cell-3-Me-PVImJ were performed in the same manner and under the same conditions as on Cell-1-Me-PVPJ and following new cellulose materials are obtained: Cellulose 3-methyl poly-1-vinylimidazole chloride (Cell-3-Me-PVImCl), Cellulose 3-methyl poly-1-vinylimidazole perchlorate (Cell-3-Me-PVImClO4), Cellulose 3-methyl poly-1-vinylimidazole trifluoroacetate (Cell-3-Me-PVImCF3COO), Cellulose 3-methyl poly-1-vinylimidazole nitrate (Cell-3-Me-PVImNO3), Cellulose 3-methyl poly-1-vinylimidazole p-tosylate (Cell-3-Me-PVIm p-TsO), Cellulose 3-methyl poly-1-vinylimidazole tetrafluoroborate (Cell-3-Me-PVImBF4) and Cellulose 3-methyl poly-1-vinylimidazole hexafluorophosphate (Cell-3-Me-PVImPF6). All synthesized cellulose-based new materials show good sorption qualities towards noble metals. Sorption of gold was thoroughly examined only on Cell-1-Me-PVPCF3. Sorption of Au was rapid and complete on it, and after 1 hour it was 99.53 wt.%, and after 24 hours was 99.89 wt.%. Capacity for Au was 0.22 g Au/g ion-exchanger and for palladium was 0.05 g Pd/g ion-exchanger. Electrochemical transformations of the anion on Lig-1-Me-PVPJ were performed under the same electrosynthesis conditions as on Cell-1-Me- PVPJ and following new materials based on lignin were obtained: Lignin 1-methyl poly-4-

vinylpyridine chloride (Lig-1-Me-PVPCl), Lignin 1-methyl poly-4-vinylpyridine perchlorate (Lig-1-Me-PVPClO$_4$), Lignin 1-methyl poly-4-vinylpyridine trifluoroacetate (Lig-1-Me-PVPCF$_3$COO), Lignin 1-methyl poly-4-vinylpyridine nitrate (Lig-1-Me-PVPNO$_3$), Lignin 1-methyl poly-4-vinylpyridine p-tosylate (Lig-1-Me-PVPp-TsO), Lignin 1-methyl poly-4-vinylpyridine tetrafluoroborate (Lig-1-Me-PVPBF$_4$) and Lignin 1-methyl poly-4-vinylpyridine hexafluorophosphate (Lig-1-Me-PVPPF$_6$). All synthesized new materials based on lignin showed good sorption qualities to noble metals but the capacities were not determend. Electrochemical transformations of the anion on Tan-1-Me-PVPJ were performed under the same electrosynthesis conditions as on Cell-1-Me-PVPJ and following new materials based on tannin were obtained: Tannin 1-methyl poly-4-vinylpyridine chloride (Tan-1-Me-PVPCl), Tannin 1-methyl poly-4-vinylpyridine perchlorate (Tan-1-Me-PVPClO$_4$), Tannin 1-methyl poly-4-vinylpyridine trifluoroacetate (Tan-1-Me-PVPCF$_3$COO), Tannin 1-methyl poly-4-vinylpyridine nitrate (Tan-1-Me-PVPNO$_3$), Tannin 1-methyl poly-4-vinylpyridine p-tosylate (Tan-1-Me-PVPp-TsO), Tannin 1-methyl poly-4-vinylpyridine tetrafluoroborate (Tan-1-Me-PVPBF$_4$) and Tannin 1-methyl poly-4-vinylpyridine hexafluorophosphate (Tan-1-Me-PVPPF$_6$). Sorption of noble metals of new tannin-based materials has not been tested. Table 4. shows numerous values of anode potential under which electrochemical transformation of grafted cellulose copolymers with 4-vinylpyrinine and 1-vinylimidazole has been carried out, as well as typical values for the anion absorption inducted into copolymer. Electrochemical cell with platinum disc electrode as working electrode was used for the study of electrochemical behavior of synthesized Cell-1-Me-PVPJ and Cell-3-Me-PVImJ in acetonitrile and tetraethylammonium perchlorate as conductive electrolyte.

Anion exchange	Solvent/Support Electrolyte(0,1M)	Applied Potential (V vs. SCE)	IR Bands (KBr)cm^{-1}
Cl-	CH_3CN/Et_4NCl	0.7	
ClO$_4$-	CH_3CN/Et_4NClO_4	0.7	1095,650
CF$_3$COO -	CH_3CN/CF_3COONa	0,7	1683,1204,834
NO$_3$-	$CH_3CN/H_2O_{(9:1)} NH_4NO_3$	1.0	1380
p-TsO -	$CH_3CN/Et_4Np-TsO$	0.7	1191,811
BF4-	CH_3CN/Bu_4NBF_4	0.7	1120,1080
PF6-	$CH_3CN/BuNPF_6$	0.7	841,558

Table 4. Electrochemical transformation of Cell-1-Me-PVPJ and Cell-3-Me-PVImJ

Cyclic voltamograms were recorded for Cell-1Me-PVPJ for a given solution composition at different mixing periods at 500 o/min. and they are shown in Fig.2. All recorded cyclic voltammograms of grafted cellulose copolymers in the ionic form show two anodic waves in the potential interval 0,35-0.65 V. Iodide ion shows two anodic waves in acetonitrile-tetraethylammonium perchlorate solution on the platinum electrode in the tested interval. The first anodic current maximum corresponds to potential of 0.35V and the second to potential of 0.65 V in relaton to SCE. The increase of the anodic waves maximum current is a result of ionic exchange reactions. Iodide is generated in reaction, as a function of time. With the extension of reaction time during the ionic exchange reaction, the amount of relased iodide increases, which is proportional to the current maximum of the first anodic wave on cyclic voltammogram in Fig. 2.
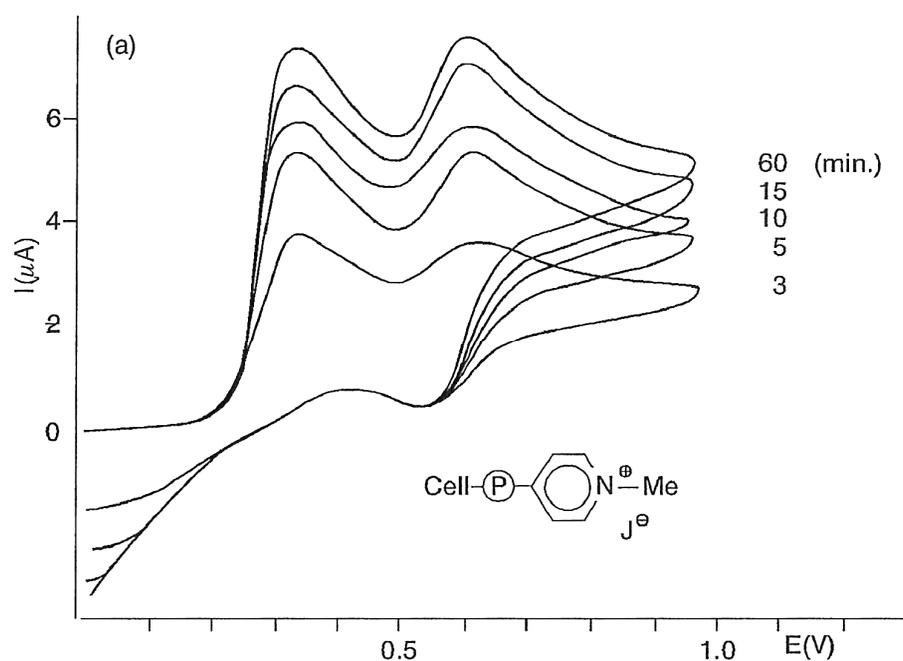
Fig. 2. Cyclic voltammograms at Pt-electrode (2r=1 mm) with scan rate of 0,1 Vs^{-1} in CH$_3$CN (25 ml)-Et$_4$NClO$_4$ (0.1 M):Cell-1Me-PVPJ (14.5 mg) at different time intervals.

Obtained cyclic voltammograms of disolved synthesized Cell-1-Me-PVPJ and Cell-3Me-PVImJ in acetonitrile in the presence of different electrolytes at different reaction times of ionic exchange are shown in Fig. 3.
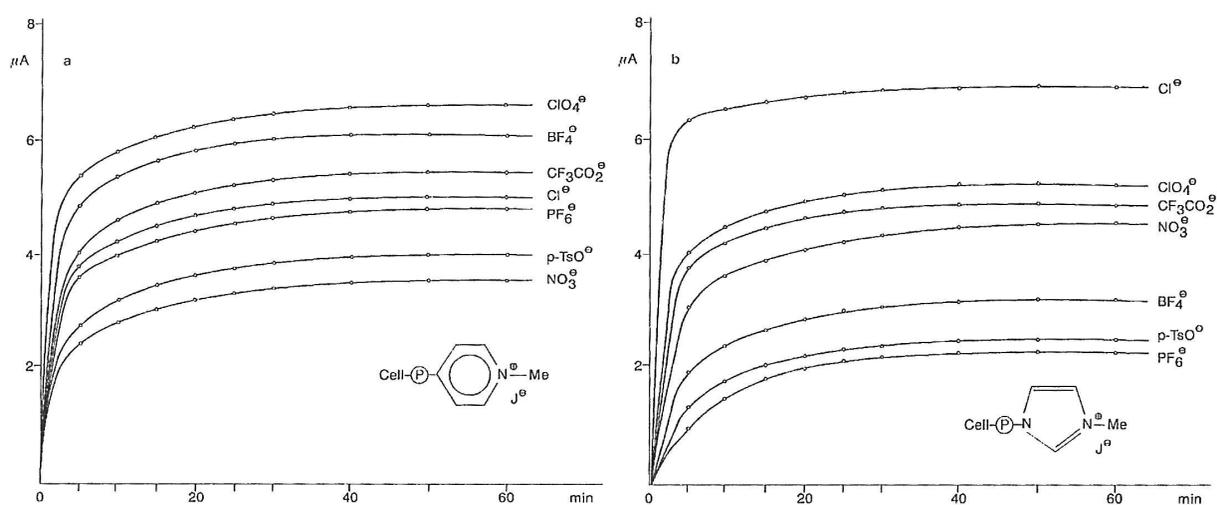

Fig. 3. Effect of time on anion-exchange reaction with the corresponding support electrolyte (0,1M) except for NH$_4$NO$_3$ (c= 0,025 M): 14,5 mg Cell-1-Me-PVPJ (a) and 14,5mg Cell-3-Me-PVImJ (b).

Curves shown in Fig. 3. indicate that the equilibrium state of iodide ionic exchange reaction with various anions is being reached after different reaction times, and that it depends on the type of anion. The amount of exchanged iodide from Cell-1Me-PVPJ and Cell-3Me-PVImJ and the concentration of basic electrolyte that displaces iodide are determined from the concentration calibration curve obtained with 1-methyl-gamma-picoline iodide and calculated

New Technology for the Synthesis of New
Materials Based on Cellulose and Sorption of Noble Metals
189

equilibrium constants for the reaction of ionic exchange. Some other factors such as rate of anion diffusion in polymer matrix and ion-pair effect affect the speed of reaction of ionic exchanges. It has been shown that this reaction is sensitive to the nature of the solvents when the reaction is carried out in the presence of other anions (Bojanic et.al., 1996; Gunic & Tabakovic,I., 1988; Tabakovic,R., et al., 1992; Tabakovic,R., & Tabakovic,I., 1999). The equillibrium can be shifted in the direction of creating products through electrochemical oxidation of exchanged iodide. Electrochemical modification of Cell-1Me-PVPJ and Cell-3Me-PVImJ into new grafted cellulose copolymers in ionic form was performed as follows: Copolymer was mixed for one hour in a given solvent-basic electrolyte system and then it was subjected to preparative anodic oxidation under corresponding controlled potential on the plateau of the second wave of the current-potential curve which was determined by a rotating disk electrode. Preparative anodic oxidation of Cell-1Me-PVPJ and Cell-3Me-PVImJ was performed at the platinum net anode (4x5 cm) as described by (Bojanic et.al, 1996). Electrolysis was stopped when current slightly fell to the residual current value and the resulting grafted cellulose copolymers in ionic form were filtered and rinsed in water, ethanol, methanol, acetone and dried at 50^0C. None of the cyclic voltammograms of the formed copolymers recorded after completion of anodic oxidation in different solutions and acetonitrile showed the presence of anodic waves of iodide oxidation, not even in traces. This means that iodide was completely replaced with other anions and grafted cellulose copolymers as ions have been formed. Typical example of such analysis is shown in Fig. 4.
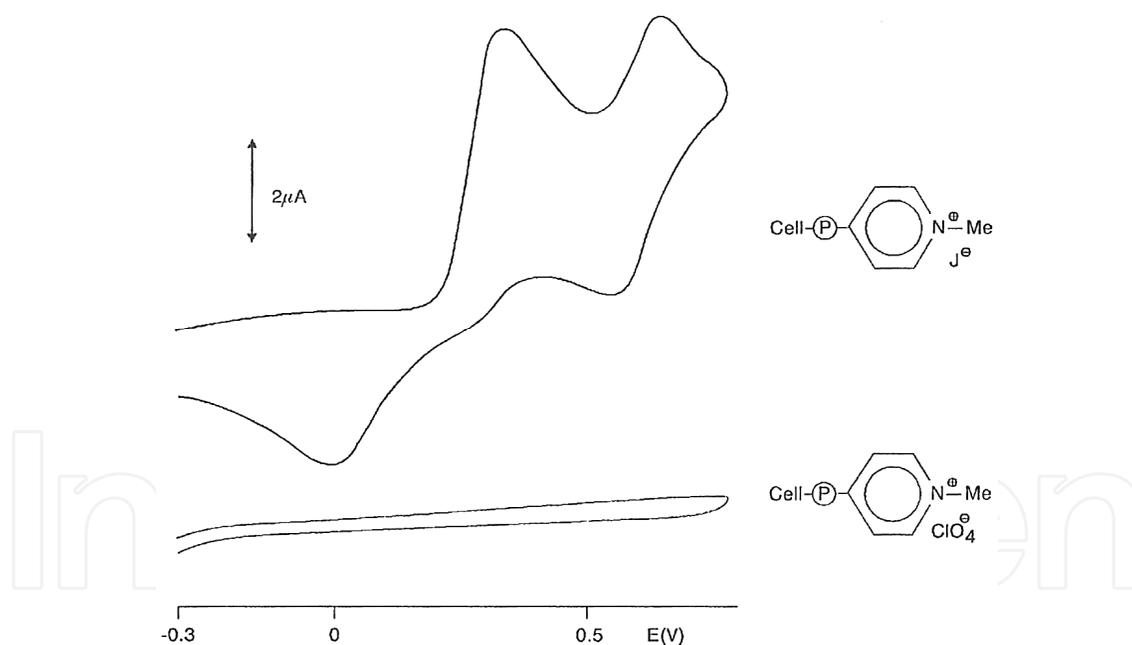

Fig. 4. Cyclic voltammograms at the Pt electrode with scan rate of 0.1 Vs^{-1} of CH$_3$CN-0,1M-Et$_4$NClO$_4$ Cell-1Me-PVPJ (14.5 mg) with iodide as a counterion and Cell-1Me-PVPClO$_4$ with perchlorate as a counterion

All synthesized grafted ionic cellulose copolymers were confirmed by IR spectroscopy and characteristic bands for the anions are shown in Table 4. The results on cellulose have shown that by simple electrochemical synthesis various new cellulose materials with 4-vinylpyridine and 1-vinylimidazole in ionic form can be obtained. New and simple methods for electrosynthesis of new materials based on cellulose, lignin and tannin have been developed

by exchanging iodide anion with the one from the basic electrolyte. New technology for the synthesis of new cellulose based materials and sorption of noble metals has been successfully applied as a model for the synthesis of new materials based on lignin (Bojanic et al., 1998b) and tannin (Bojanic & Jovanovic, 2000). Following new cellulose based materials are synthesized with these new technologies: Cellulose acrylate, Cellulose-poly-1-vinyl-2-pyrrolidone, Cellulose-poly-9-vinylcarbazole, Cellulose-poly-4-vinylpyridine, Cellulose-poly-vinylimidazole, Cellulose-1-methylpoly-4-vinylpyridine iodide, Cellulose-3-methylpoly-1-vinylimidazole iodide, Cellulose-1-methylpoly-4-vinylpyridine perchlorate, Cellulose-1-methylpoly-4-vinylpyridine trifluoroacetate, Cellulose-1-methylpoly-4-vinylpyridine tetrafluoroborate, Cellulose-1-methylpoly-4-vinylpyridine chloride, Cellulose-1-methylpoly-4-vinylpyridine hexafluorophosphate, Cellulose-1-methylpoly-4-vinylpyridine p-tosylate, Cellulose-1-methylpoly-4-vinylpyridine nitrate, Cellulose-3-methyl poly-1-vinylimidazole perchlorate, Cellulose-3-methylpoly-1-vinylimidazole tetrafluoroborate, Cellulose-3-methylpoly-1-vinylimidazole trifluoroacetate, Cellulose-3-methylpoly-1-vinylimidazole chloride, Cellulose-3-methylpoly-1-vinylimidazole hexafluorophosphate, Cellulose-3-methylpoly-1-vinylimidazole p-tosylate, Cellulose-3-methylpoly-1-vinylimidazole nitrate. Also, with this new technology following new materials based on lignin have been synthesized: Lignin acrylate, Lignin-poly-4-vinylpyridine, Lignin-1-methylpoly-4-vinylpyridine iodide, Lignin-1-methylpoly-4-vinylpyridine trifluoroacetate, Lignin-1-methylpoly-4-vinylpyridine tetrafluoroborate, Lignin-1-methylpoly-4-vinylpyridine perchlorate, Lignin-1-methylpoly-4-vinylpyridine tosylate, Lignin-1-methylpoly-4-vinylpyridine hexafluorophosphate, Lignin-1-methylpoly-4-vinylpyridine chloride, Lignin-1-methylpoly-4-vinylpyridine nitrate; and new materials based on tannin: Tannin acrylate, Tannin- poly-4-vinylpyridine, Tannin-1-methylpoly-4-vinylpyridine iodide, Tannin-1-methylpoly-4-vinylpyridine perchlorate, Tannin-1-methylpoly-4-vinylpyridine tetrafluoroborate, Tannin-1-methylpoly-4-vinylpyridine trifluoroacetate, Tannin-1-methylpoly-4-vinylpyridine chloride, Tannin-1-methylpoly-4-vinylpyridine hexafluorophosphate, Tannin-1-methylpoly-4-vinylpyridine p-tosylate, Tannin-1-methylpoly-4-vinylpyridine nitrate.

4. Thermogravimetric and ion-exchanging properties of new cellulose based materials

4.1 Thermogravimetric analysis of cellulose copolymers grafted with 4-vinyl pyridine in ionic form

Thermal degradation of lignocellulosic material is not simple, but rather very complex process because it takes place through series of complex chemical reactions (Simkovic, 2007). This reaction is largely affected by nature of bonds and period of heating, the atmosphere in which it occurs, inorganic impurities and non-cellulose components (Ibrahim et al., 2011). Grafted cellulose copolymers, which have ion-exchanging qualities, represent materials that are showing different behavior during exposure to heating, depending on the nature of ion species within. Thermal degradation of cellulose, cellulose acrylate and some of its grafted copolymers in ionic form has been studied: Cell-PVP, Cell-1Me-PVPJ,Cell-1-Me-PVP·ClO$_4$, Cell-1-Me-PVPPF$_6$, Cell-1-Me-PVPBF$_4$, Cell-1-Me-PVPCF3COO, Cell-1-Me-PVPp-TsO, Cell-1-Me-PVPCl, Cell-1-Me-PVPNO$_3$ (Bojanic et al., 1997). Cellulose loses adsorbed and chemisorbed water when heated in the temperature interval from 50^{0}C to 120^{0}C. By further heating this absolutely dry cellulose does not change mass until temperature reaches 300^{0}C,

New Technology for the Synthesis of New
Materials Based on Cellulose and Sorption of Noble Metals
191

when very slow mass loss begins. This is referred as the first period of thermolysis of cellulose during which its depolymerization ocurs. Sudden loss of weight, the second period of thermolysis between 360 and 425°C, is followed by formation of series of gaseous products. At temperatures above 425°C, there is slow loss in weight, since already charred and probably crosslinked lignocellulosic residue material finishes its degradation and transfers to gaseous phase. This is known as the third period of thermolysis. In reaction between acryloyl chloride and cellulose and by its grafting with 4-vinylpyridine, the chemical composition and the degree of order in structures of the initial cellulose is changing. When heated in the inert atmosphere and after losing adsorbed and chemisorbed water at temperatures above 120°C synthesized cellulose acrylate and Cell-PVP show similar response as the initial cellulose. Perkin Elmer TGS-2 thermogravimetry apparatus was used to determine thermal stability of tested cellulose materials. Experiments were conducted in nitrogen atmosphere at gas flow of 45 cm^3/min, the heating rate of 10^0C/min, and samples weights were 5 mg. The values for the mass residue were read off (m/m_ox 100) at 200, 270, 340, 410, and 480^0C, temperatures where the mass loss (m_o -m/m_ox100) was 10, 50, 90 and 100 wt. %, and temperature fields in which I , II, and III period of cellulose thermolysis happened. These data for cellulose acrylate and Cell-PVP are shown in Table 5.

Materials	Rest of mass m/m_o%, T^0C					Loss of mass				T^0C, Thermolysis period		
	200	270	340	410	480	10	50	90	100	I	II	III
Cellulose	95	94.5	93	27	8	360	400	425	616	300-360	360-425	425-600
Cell-akrilate	93	90	80	33	25	285	375	580	682	200-340	340-380	380-640
Cell-PVP	94	91.5	73	31	29	290	355	620	739	130-330	330-360	360-730

Table 5. TGA results for cellulose, Cell- acrylate and Cell-PVP

Thermolysis of cellulose and Cell-PVP occurs in three stages after loss of adsorbed and chemisorbed water at temperatures up to 120^0C. The first period of thermolysis starts at lower temperatures than cellulose, at $270-300^0C$. The second period of thermolysis begins and ends at lower temperatures, $330-380^0C$, with lower mass loss of 50% than with cellulose: $340-400^0C$, loss of 80 wt%. Period of slow weight loss up to complete degradation, unlike cellulose in which this is happening in the temperature range of $410-600^0C$, is extended to $340-730^0C$. The reduction of thermal stability of cellulose acrylate and Cell-PVP compared to cellulose in the first period of thermolysis is reflected in smaller quantity of non-reacted sample at the same temperature. The second period of thermolysis takes place in more narrow interval $330-380^0C$ than with cellulose $360-425^0C$. This is due to greater accessibility of amorphous structures of cellulose derivatives and weaker hydrogen bonds in cellulose macromolecule, and it is assumed to be limiting step of the overall reaction of thermal decomposition. In terms of reaction in the third period, an increased amount of charred cellulose acrylate and significantly slower weight loss can be attributed to crosslinking of the structure, which increases the pyrolytic stability and that can be observed with non-substituted cellulose, as well. In the case of cellulose acrylate additional crosslinking of charred cellulose residue can be expected due to reactions of vinyl groups and their derivatives during thermolysis. Crosslinking of Cell-PVP structure contributes to more difficult diffusion of gaseous degradation products and their retention, i.e. binding with charred residue, hence the weight of the residue is declining even slower and the temperature at which thermolysis was

completed is greater, 730^0C. This indicates increased stability of the cellulose after grafting (Barsbay et al. 2007). With non-substituted cellulose, but also in the case of thermolysis of cellulose derivatives in ionic form, limiting step is process of tearing off glycosidic bonds (Simkovic, et al., 1985). Although chemical composition compared to cellulose is altered, observed copolymers show three-step mass loss characteristic for cellulose and Cell-PVP. Cell-1-Me-PVPCF$_3$ and Cell-1-Me-PVPBF$_4$ show deviation from this type of reaction. They have multiple-response. Table 6. shows the results of thermolysis of the observed materials. Data were collected from corresponding TGA-curves.

Materials	Rest of mass m/m$_o$ %					T^0C					Thermolysis period		
	T^0C						Loss of mass						
	130	200	270	340	410	480	10	50	90	100	I	II	III
Cell-1Me-PVPCF$_3$COO	96	95	85	64	31	26	247	350	600	760	143-275	275-340	340-355
Cell-1Me-PVPBF$_4$	93	93	90	71.5	46	39	270	367	633	760	120-325	325-377	377-660
Cell-1Me-PVPCI	95	92	90	66	33	27	270	345	595	650	120-270	270-377	377-660
Cell-1Me-PVPJ	95.3	95	94	82	32	27	287	350	610	710	250-350	350-520	520-710
Cell-1Me-PVPNO$_3$	96.5	92	90	64	33	28	272	344	605	710	140-270	270-380	380-710
Cell-1Me-PVPPF$_6$	95	95	93	54.2	49	44	290	405	740	760	140-270	270-310	310-600
Cell-1Me-PVP$_P$-T$_S$O	95	94	91	51	43	37	275	346	625	700	140-270	270-380	380-509
Cell-1Me-PVPClO$_4$	96	95	93	24	22	18	300	305	445	655	130-270	270-35	305-665

Table 6. TGA results of grafted cellulose copolymers in ionic form

Non-reacted residue of all cellulose copolymers in ionic form at 270^0C is 90-94 wt.% and it is similar to Cell-PVP which equals 91wt.%. The exception is very unstable Cell-1-Me-PVPCF$_3$COO which has smaller non-reacted residue of 85.4wt.%. However, the mass loss of the first 10% of initial air dried cellulose sample takes place at lower temperatures than that of Cell-PVP. Out of these 10wt.%, around 5-7wt.% goes to moisture. The temperature of the 10% mass loss declines in the following manner: Cell-1-Me-PVPClO$_4$>Cell-PVP>Cell-1-Me-PVPp-TsO >Cell-1-Me-PVPNO$_3$>Cell-1-Me-PVPCI = Cell-1-M-PVPBF$_4$>Cell-1-Me-CF$_3$COO. This also presents thermal stability of cellulose copolymers in ionic form. All observed samples are more susceptible to degradation during heating then Cell-PVP, except for Cell-1Me-PVPClO$_4$ and Cell-1Me-PVPBF$_4$, which show increased stability. The first period of thermolysis takes place in a narrower temperature interval than Cell-PVP for all ion forms without exception. The second period of thermolysis with rapidly declining mass is the fastest in case of Cell-1Me-PVPClO$_4$, which loses 40% of weight at temperatures of 300-305°C, while other samples are losing mass slower. According to the amount of non-reacted residue at 340^0C they can be ranked in order: Cell-1-Me-BF$_4$ >Cell-1-Me-PVP CI > Cell-1-Me-PVP CF$_3$OO = Cell-1-Me-

$PVPNO_3$ > Cell-1-Me-PVPPF6 > Cell-1-Me-PVPp -T_sO > Cell - PVP >Cell-1-Me-PVPCIO$_4$. According to the mass of charred residue at this temperature, all observed grafted cellulose copolymers in ionic form, apart from the most unstable Cell-1-Me-PVPCIO$_4$, have higher amount of residue of 51-71wt.%. In comparison, Cell-PVP has non-reacted residue of 31wt.%. The rate of mass loss of Cell-1-Me-PVPPF$_6$, Cell-1-Me-PVPBF$_4$ and Cell-1-Me-PVPp-TsO$_4$ is smaller and of Cell-1-Me-PVPCF$_3$COO, Cell-1-Me-PVPNO$_3$, Cell-1-Me-PVPCl is similar to the one of charred Cell-PVP. The amount of charred residue at 480°C decreases in the following order: Cell-1-Me-PVPPF$_6$ > Cell-1-Me-PVPp-TsO > Cell-PVP > Cell-1-Me-PVPNO$_3$ = Cell-1-Me-PVPCl > Cell-1-Me-PVPCF$_3$COO > Cell-1-Me-PVPClO$_4$. Introduction of ion types in Cell-PVP decreases the thermal stability of new cellulose materials.

4.2 The application of new grafted cellulose and lignin copolymers for the selective sorption of noble metals

The application of synthesized grafted cellulose and lignin copolymers for selective extraction of gold, palladium and platinum from the solution with other metals was done (Bilba et al., 2010; Bojanic et al., 1998c, 2001; Dubiella-Jackowska et al., 2007; Liu et al., 2000; Masllorens et al., 2006; Nastasovic et al., 2006; Navarro et al., 2006; Othman et al., 2005; Sandic & Nastasovic, 2009; Tavlarides et al., 2006). Following copolymers synthesized for this purpose were used: Cell-PVP, Cell-1-Me-PVPJ, Cell-1-Me-PVPCF$_3$COO, Cell-PVIm, Lig-PVP and Tan-PVP. Three series of experiments were conducted and tests were performed at the Institute for Copper-RTB Bor Serbia. The determination of the amount of gold and palladium related to new cellulose and lignin materials has been carried out with Perkin Elmer Company, model 703 atomic absorption spectrophotometer with measurement accuracy of 0,001µgAu/dm^3. In the first series of experiments, the sorption of gold from the solution has been examined on: Cell-PVP, Cell-1Me-PVPJ, Cell-1Me- PVPCF$_3$COO. Gold solution for these tests was obtained by dissolving pure gold in aqua regia. After dissolution of gold, excess of nitric acid was eliminated from the solution by evaporation. HAuCl$_4$ solutions have been made with different content of gold and different pH values by dilution with bidistilled water. All new materials based on cellulose and lignin were treated the same way. Gold solution with concentration of 4.32g/dm^3 and pH=1.55 was used to study sorption of gold in these cellulose copolymers. 0.1g of cellulose copolymers were placed in 3 cm^3 of initial gold solution and the content of gold was measured before the placement, after 1h and 24h. All experiments were performed at room temperature. Since the degree of Au sorption on all the samples exceeded the value of 99 wt.%, sorption was good and it was practically carried out in 1 hour time. The capacity, g Au/g ion-exchanger for all cellulose copolymers, as well as for lignin and tannin copolymers. The solution originating from the industrial processing of anodic sludge from the stage of obtaining gold by the process of electrolytic refining in RTB Bor-Serbia was used. An electrolyte that can still be used, which contains 120g of gold, platinum, palladium, copper and iron/dm^3 was used to determine the capacity of the samples. In this solution, gold is present in the form of HAuCl$_4$, platinum and palladium in the form of H$_2$PtCl$_6$ and H$_2$PdCl$_6$ and the capacity was determined in the same manner as the degree of sorption: Cell -PVP-0.2g Au/1g ion-exchanger, Cell-1Me-PVPJ-0.24g Au/1g ion-exchanger Cell-1Me-PVPCF$_3$COO-0.22g Au/1g ion-exchanger and Cell-PVIm-0.23g Au/1g ion-exchanger Lig-PVP-0.4Au/1g ion-exchanger and 0.2g Pd/1g ion-exchanger. Regeneration of ion-exchanged Lig-PVP with HCl (1:1) was complete. However, characteristics after regeneration were not tested. Sorption of platinum is very

good. It was not possible to examine Tan-PVP for the sorption of Au, since it is water-soluble. In the third series of experiments the aim was to examine certain characteristics of Cell-PVP such as capacity, level of sorption, period of sorption and selectivity in details. The solution originated from the industrial production in RTB Bor-Serbia, as in the second series, so Cell-PVP could be used for commercial purposes. New sorption materials for selective extraction of noble metals were applied in a continuous and batch mode. In batch experiments, calculated quantities of grafted copolymer were continuously mixed with the solution from which it was necesary to selectively extract certain noble metals, primarily gold. Sorbent was than separated and the noble metal was eluted in the same way, but with much smaller quantity of hydrochloric acid. Columns with the sorbent were used in a continuous mode. Sorption and desorption were conducted principally in the same manner as in batch experiments. 0.1M solution with gold concentration of 19.25g Au/dm^3 and pH=1.2, as well as 0.1 M solution with palladium concentration of 10.64g Pd/dm^3 and pH=0.28 were used to test the degree of sorption, capacity, period of sorption and selectivity. The results of such tests have been confirmed in the same way as in first and second series of experiments. The regeneration with HCl (1:1) has been studied and it was found that 0.1g of Cell-PVP ion-exchanger sorbed 0.1g of gold, which is twice less than the actual capacity, hence confirming that there has been a decline in its sorption power by 50 wt.%. The selectivity of Cell-PVP in the solution of gold, platinum and palladium has been studied with the presence of copper and iron, and it was shown that there is no sorption of non-noble metals. Grafted cellulose and lignin copolymers have, on one hand, the characteristics of the electron exchangers and, on the other hand, characteristics of complexes with high degree of selectivity. They have been used as new cellulose and lignin materials for noble metal ions containing wastewater treatments for chemical and electronic industries (Alguacil, 1998; Al-Merey et al., 2003; Azarudeen et al., 2009; Chang &Chen, 2006; Farang et al., 2007; Hussain & Khan 2011; Ladhe, 2008; Liu, et al., 2009; Nguyen et al., 2010; O Malley, 2002; Ran et al., 2002; Zhong et al., 2007). Chemical and electrochemical modification of cellulose and lignin is based on synthesis of new materials with 4-vinylpyridine or similar vinyl derivatives of heterocyclic skeleton with at least one nitrogen atom, and they were used as specific chemisorbents of noble metals ions from dissolved aqueous solutions. New technology for the synthesis of new materials based on cellulose and sorption of noble metals is confirmed in industrial production in RTB Copper Institute, Bor-Serbia. Sorption of noble metals is quick and complete. Au, Pd and Pt, as nanoparticles, directly implement into the matrix of biopolymers, and they are producing chelating complexes and ligands by chemisorption with a new structure of biopolymers in this way. Capacities are 20 wt.% higher than standard commercial products of world famous companies. They are outstandingly selective in relation to Fe and Cu and they can sorb very small concentrations of Au, Pd and Pt from the solution which gives them a complete ecological and economic feasibility and the advantage compared to existing technologies. Their special value in fundamental research is that bionanonoblemetals polymers are synthesized for use in nanoelectronics (Bloor et al., 2005, 2006; Burda et al., 2005; Cao et al., 2009; Dai et al., 2006; Feng et al., 2010; Hoppe et al., 2006; Ingrosso et al., 2010; Kim et al., 2007; Lai et al., 2008; Lazzari & Lopez-Quintela, 2003; Li et al., 2010; Liu, T et al., 2003; Liu, P. et al., 2009; Sarkar et al., 2010; Sathishkumar et al., 2009; Thompson, 2007; Yaghi et al., 2003; Yin et al., 2009; Yoon et al., 2008; Zhang et al., 2009; Zubarev et al., 2006) and cancer nanotechnology (Cai et al., 2008; Chen et al., 2008; Daniel & Astruc, 2004; De et al., 2008; Patraet al., 2007; Popovtzer et al., 2008; Xia et al., 2003; Yang et al., 2008; Love et al.,2005).

5. Future researches

For centuries, electrochemistry has played a key role in technologically important areas such as electroplating or corrosion. Electrochemical methods are receiving increasing attention in rapidly growing fields of science and technology, such as nanosciences (nanoelectrochemistry) and life sciences (organic and biological electrochemistry). Characterization, modification and understanding of various electrochemical interfaces or electrochemical processes at the nanoscale level have led to a huge increase of scientific interest to novel technologies. Electrochemical methods carried out at the nanoscale level lead to exciting new science and technology. Hence, trends in electrochemistry are leading to experiments obtaining ever smaller particles in seminano and nanoscale range.

Some applications of cellulose-based materials are either more economically profitable or require its use in the form of conductive composites. Natural polymers based on renewable materials with addition of chosen materials can be directly used as contemporary materials by electrochemical methods (Bojanic et al., 1996, 1998b, 2000). Tailoring new composites within a perspective of sustainable development is applied to more and more materials. Ecological concerns have resulted in a renewed interest in natural, renewable resources-based and compostable materials, and therefore issues such as materials elimination and environmental safety are becoming important. For these reasons, material components such as natural fibers, biodegradable polymers obtained from biomass can be considered as ''interesting''–environmentally safe–alternatives for the development of new biodegradable composites (Bojanic, 1994, 2010). These polymers show a large range of properties and at present, they can compete with non-biodegradable polymers in different industrial fields (Bojanic, et al., 1988a, 1998c, 2001). Lignocellulosic feedstocks are composed primarily of carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin). Lower concentrations of various other compounds, such as proteins, acids, salts and minerals, are also present. Both cellulose and hemicelluloses have favorable properties for potential use in the biomedical area, as they have the ability to pass through the digestive tract unchanged. Owing to their resistance to digestion, they are eligible as potential excipients that could be used in the pharmaceutical industry. Information about numerous existing possibilities of polymers containing dispersed conductive fillers and various methods of manufacture of such materials have been reported widely in the literature (Pinto et al., 2011). Also they found numerous technological applications as self regulating heater, photothermal optical recording, direction finding antennas, chemical detecting sensors used in electronic noses, chemical and electrochemical catalysts and adsorbents . The electrolytic powder production method usually allows products of high purity which can well be pressed and sintered. Besides, in recent years it has been shown that by different electrolysis regimes it is possible not only to obtain powders with a wide range of properties, but to predict the decisive characteristic of powders which are of vital importance for the powder quality and for the appropriate purpose. (Pavlović, M.G. & Popov, K.I., 2005; Popov, K.I. & Pavlović, M.G., 1993).

For metal powder application, a series of their properties are of interest; the size and shape of the particles, the bulk weight, flow rate, the corrosion resistance, the specific surface area, the apparent density and the quality of the sintered products. Finally, the properties mentioned depend on the shape and the size of the particles which can be influenced by electrolysis regimes (Pavlović et al., 1998, 2010; Pavlović, M.G. & Popov,

K.I., 2005; Popov & Pavlović, M.G, 1993). Generally speaking, the larger the powder specific surface the lower its apparent density, and all the more so the smaller the particle size. On the other hand, it seems to be that particle structure has the vital importance on apparent density and on the powder quality. The method most often employed to alter the electrical properties of a polymer is an extrinsic approach whereby the insulating polymer is combined with a conductive additive. The electrical conductivity of polymer composites does not increase continuously with increasing electroconductive filler content. Hence, in general, the percolation theory is used to describe the nonlinear electrical conductivity of extrinsic conductive polymer composites. The conducting additive is incorporated into polymers at levels that allow the composite to maintain its electrically insulative qualities, as well as at higher levels, which allow the composite to become electrically semiconductive. As the volume fraction of the conducting filler particles increases, the particles come into contact with one another to form the conduction paths through the composite. As the result there is a critical composition (percolation threshold) at which the conductivity increases by some orders of magnitude from the insulating range to values in the semiconductive or metallic range (Pinto et al., 2011). The conductivity of filled polymers is strongly dependent on the nature of the contact between the conductive filler elements. Therefore, the copper powder was galvanostatically produced since it has distinct dendritic morphology and large specific area (Pavlović, M.G. et al., 1998, 2010; Pavlović, M.G. & Popov, K.I. 2005, Popov & Pavlović, M.G, 1993). The electrical conductivity measurements as a function of filler content (copper powder-Fig. 5) showed typical *S*-shaped dependency with three distinct regions: dielectric, transition and conductive (Pavlović, M.M et al., 2011).
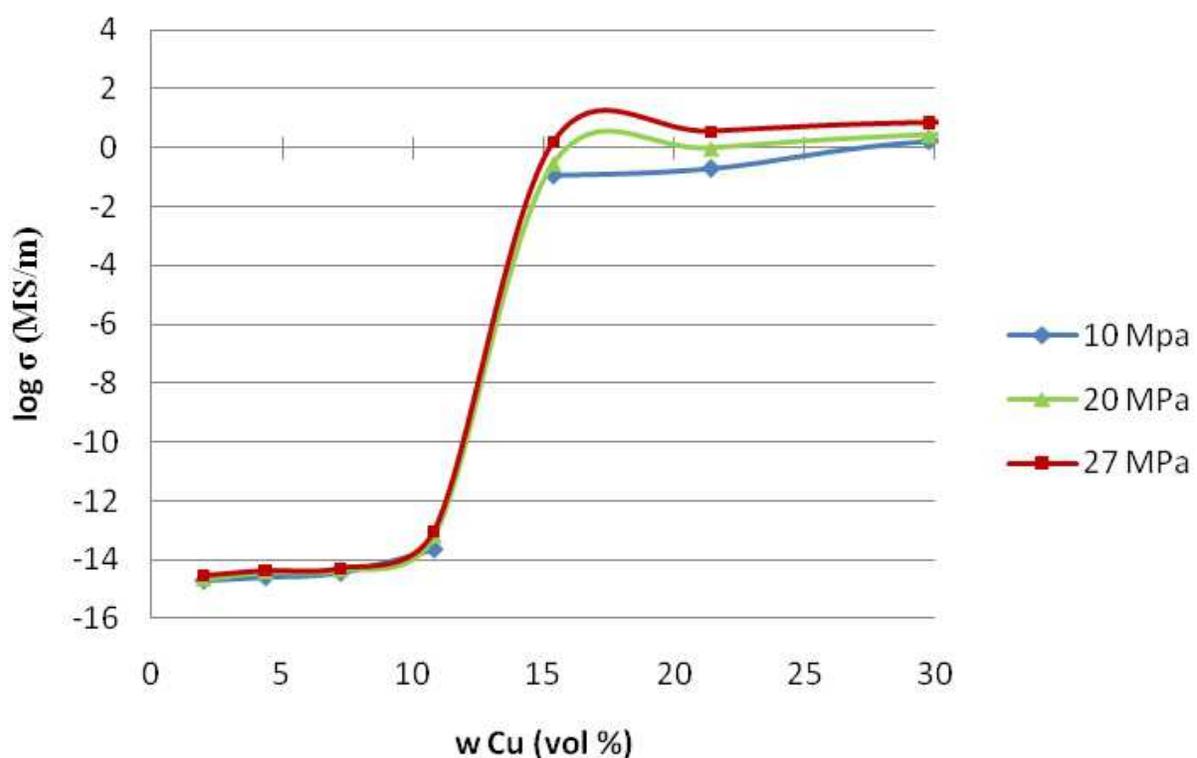

Fig. 5. Variation of electrical conductivity, as a function of filler content, of lignocellulose composites filled with copper powder under different processing pressures (Pavlović, M.M. et al., 2011).

Clearly, the samples with low filler content are practically nonconductive. Naturally, the electrical conductivity of the composites increases with the increase of the conductive filler content. The significant increase of the electrical conductivity can be observed as the copper content reaches the percolation threshold at 14.4% (v/v) for all the processing pressures. The value of the percolation threshold was obtained from of the maximum of the derivative of the conductivity as a function of filler volume fraction (Fig. 5). However, in the conductive region, composites with the same volume fraction of copper powder prepared under higher pressure have higher values of conductivity. Above the percolation threshold, the conductivity of composite increased by much as fourteen orders of magnitude (Pavlović, M.M. et al., 2011). In any case, when considering electroconductive polymer materials, it is desirable to thoroughly examine not only galvanostatically obtained copper powder as filler, but also copper powder obtained by other electrochemical procedures, as well as the effect of different deposition regimes, on the powdered metal electrodeposits morphology in order to obtain nanoscale powders. Above all, electrodeposition of metal powders, suchs as silver, gold, palladium, platinum, zinc, tin, etc., at a periodically changing rate (pulsating overpotential and reversing, and pulsating currents) should be examined. The purpose of this future researches will be to present a possibility of electrodeposition of metal powders with contolled grain size, morphology, and crystal structure of the particles. Morphology is probably the most important property of electrodeposited metals. It depends mainly on the kinetic parameters of the deposition process and the deposition overpotential or current density. In general, they depend on the shape and the size, which can be influenced by appropriate electrolysis regime. The assumption for the silver powder (Dimitrov et al., 1998; Maksimovic et al., 2007; Pavlović, M.G. et al., 1978; Popov et al., 1978, 1991, 1996, 1998; Radmilovic et al., 1998; Strbac et al., 1999) is that all effects which can be obtained by changing parameters determining the deposition regime in direct current deposition conditions can be obtained by changing the shape of the current or overpotential wave only in electrodeposition at a periodically changing rate. Furthermore, at the same time, the surface crystal structure of powder particles can be varied from polycrystalline to one characterized by well-defined crystal planes.Noble metals powder particles obtained in this way used with natural polymers based on renewable materials can be directly used as contemporary materials by electrochemical methods, and they will be able to satisfy different requirements. Such new materials obtained by the new technology are bionanonoblemetals biopolymers with nanoparticles of noble metals, and they can be used in nanoelectronics and cancer nanotechnology which is the subject of current and future researches. This will be of great benefit to many emerging technologies involving molecular electronics, miniature fuel cells, chiral catalysis and biomaterials with hybrid properties.

6. Conclusions

Procedure for the synthesis of cellulose acrylate has been developed and it has been successfully applied for the synthesis of lignin and tannin acrylate. The impact of the relations of the reactants: cellulose, potassium-t-butoxide, acyiloyl chloride and reaction period on the yield of cellulose acrylate has been thoroughly examined. The optimum synthesis conditions under which the cellulose acrylate is obtained with DS 2.4 and Y-80.7 is achieved when the ratio of reactants cellulose/potassium-t-butoxide/acryloyl chloride

= 1:3:10, and the reaction time is 10 hours. Radical copolymerization of synthesized cellulose, lignin and tannin acrylates with 4-vinylpyridine, 1-vinylimidazole, 9-vinylcarbazole and 1-vinyl-2-pyrrolidine yields grafed copolymers and polymers: Cell-PVP, Cell-PVIm, Cell-P9VK, Cell-P1V2P, Lig-PVP, Tan- PVP. In reactions of quaternization of grafted Cell-PVP, Cell-PVIm, Lig-PVP and Tan-PVP copolymers with methyl iodide following polymers were synthesized: Cell-1Me-PVPJ, Cell-3Me-PVImJ, Lig-1Me-PVPJ, Tan-1Me-PVPJ. Cyclic voltammetry method was used to investigate electrochemical behavior of synthesized: Cell-1Me-PVPJ, Cell-3Me-PVImJ, Lig-1-Me-PVPJ and Tan-1Me-PVPJ. Constant current regime electrolysis was used for substitution of iodide anion with anion present in the basic electrolyte from formerly mentioned copolymers. New materials based on cellulose were synthesized: Cell-1-Me-PVPClO$_4$, Cell-1-Me-PVPCl, Cell-1-Me-PVPCF$_3$COO, Cell-1-Me-PVPNO$_3$, Cell-1-Me-PVPp-TsO, Cell-1-Me-PVPBF$_4$, Cell-1-Me-PVPPF$_6$, Cell-3-MePVImClO$_4$, Cell-3-Me-PVImCl, Cell-3-Me-PVImCF$_3$COO, Cell-3-Me-PVImNO$_3$, Cell-3-Me-PVImp-TsO, Cell-3-Me-PVImBF$_4$ and Cell-3-Me-PVImPF$_6$. In the same manner new materials based on lignin were synthesized: Lig-1-Me-PVPClO$_4$, Lig-1-Me-PVPCl, Lig-1-Me-PVPCF$_3$COO, Lig-1-M-PVPNO$_3$, Lig-1-Me-PVPp-TsO, Lig-1-Me-PVPBF$_4$ and Lig-1-Me-PVPPF$_6$ as well as new tannine based materials: Tan-1-Me-PVPClO$_4$, Tan-1-Me-PVPCl, Tan-1-Me-PVPCF$_3$COO, Tan-1-Me-PVPNO$_3$, Tan-1-MePVPpTsO, Tan-1-Me-PVPBF$_4$ and Tan-1-Me-PVPPF$_6$. Thermal stability of some synthesed cellulose copolymers in ionic form was tested by thermogravimetry method and it was compared with the stability of pure cellulose acrylate, cellulose, and Cell-PVP. Cellulose copolymers in ionic form have lower thermal stability than pure cellulose and the type of anion present in the copolymer has a decisive influence on their behavior at elevated temperatures. The application of the following synthesized new materials was studied: Cell-PVP, Cell-1Me-PVPJ, Cell-1Me-PVPCF$_3$COO, Cell-PVIm and Lig-PVP as ion-exchangers for sorption of noble metals from aqueous solutions. These copolymers can selectively extract gold, platinum and palladium from solutions containing copper and iron. The degree of gold sorption from clean solutions for Cell-PVP, Cell-1Me-PVPJ and Cell-1Me-PVPCF$_3$COO is from 99.03 to 99.89 wt.%, capacity for Au from 0.20 to 0.40 g Au/g ion-exchanger. Capacity for Pd is 0,20g/ Pd g ion-exchanger and sorption of platinum is good. These values are 20 wt. % higher than standard commercial products of world famous companies, which are used to bind ions of noble metals from aqueous solutions. Selectivity of obtained ion-exchangers is of particular iterest from the theoretical and technical point of view. They are completely indifferent to copper and iron ions. New technology has been successfully applied for the synthesis of new materials based on lignin and tannin. It can be used for obtaining acrylate biopolymers. Biopolymers are copolymerized with a 4-vinylpyridine or similar vinyl derivative with heterocyclic skeleton and at least one nitrogen atom. Nitrogen atom is quaternized with methyl iodide and obtained material is electrochemicaly transformed whereby the iodide anion is replaced by another. Synthesized new materials are used as selective sorbents for the extraction of noble metals from diluted aqueous solution, especially gold. Such new materials obtained by the new technology are bionanonoblemetals biopolymers with nanoparticles of noble metals, and they can be used in nanoelectronics and cancer nanotechnology which is the subject of current and future researches. This will be of great benefit to many emerging technologies involving molecular electronics, miniature fuel cells, chiral catalysis and biomaterials with hybrid properties.

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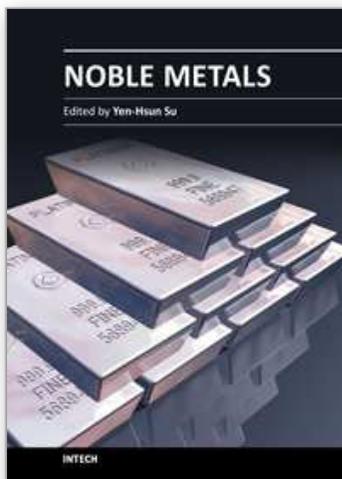
This book provides a broad spectrum of insights into the optical principle, resource, fabrication, nanoscience, and nanotechnology of noble metal. It also looks at the advanced implementation of noble metal in the field of nanoscale materials, catalysts and biosystem. This book is ideal not only for scientific researchers but also as a reference for professionals in material science, engineering, nonascience and plasmonics.

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