SUMMARIES OF MAIN SCIENTIFIC RESULTS AND SCIENTIFIC CONTRIBUTIONS

Assist. Prof Temenuzhka Hristova Radoykova, Department Analytical Chemistry, UCTM

The research I have conducted, described in the scientific publications with which I participate in the competition, is multidisciplinary in nature, but can be classified in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2 Chemical Sciences, scientific specialty "Analytical Chemistry (Instrumental Methods of Analysis)", since I apply a wide range of chemical and instrumental methods to solve problems of fundamental and ecological importance. Analytical approaches have been applied for the characterization and utilization of biomass waste products (hydrolysis lignocellulosic materials, bark); waste and secondary products from metallurgical production (tail, blast furnace slag); waste product from coal-fired power plants (fly ash). A key point in my work is the application of gas chromatography (GC-MS; GC-FID) for the analysis of low-molecular phenolic compounds with potential for their use as antioxidants.

This author's reference is based only on the declared scientific publications for participation in the competition for the academic position of "Associate Professor" 28 in number (8 publications are declared in indicator 4 and 20 publications in indicator 7), 19 of which are published in publications with impact factor (IF); 4 with impact rank (Scopus), 3 are in proceedings of scientific conferences, presented in Conference Proceeding in Scopus and Web of Science, and 2 are in Conference Proceeding with ISSN number.

The publications included in the dissertation for the degree of doctor (author's abstract) will not be considered in this reference for the scientific contributions of the works participating in the competition. However, they marked one of the main directions of my subsequent scientific interests, namely the preparation, isolation and characterization of useful products (low molecular weight phenolic compounds, absorbents and biocoke) from waste lignocellulosic materials.

In 20 publications participating in the competition (71%) I am the first author or second author. I have participated in the implementation of 23 projects, including as a mentor in Project BG05M2OP001 -2.013-0001 "Student Practices - Phase 2" and 5 projects at the National Science

Foundation. I have been the manager of 9 contracts at NIS-HTMU and one active sub-project to project BG-RRP-2.004-0002-C01, BiOrgaMCT, 12.2023.

For the last 5 academic years, I have an average annual study load of over 350 hours.

Under my supervision, 6 diploma theses for the "Master" degree in "Applied Analytics" have been prepared and defended. I have also been a consultant to 6 graduates of the bachelor's and master's degree programs at the Department of Pulp, Paper and Printing.

Summary of the scientific papers:

Total number of scientific papers submitted for participation in the competition: 28

Total impact factor: 20.00

Individual impact factor: 4.52

h-index: 9

- 1. Publications in refereed journals in the Scopus and Web of Science databases with impact factor or impact rank
 - A. with impact factor: 19
 - B. with impact rank: 4
 - C. Conference Proceeding in Scopus and Web of Science: 3
 - 2. Conference Proceeding with ISSN number: 2
 - 3. Participation in other scientific forums (reports/posters)> 27
 - **4. Total number of citations noted** >283 (Scopus).

Indicator	Scientific journal	Year of	Year Indexing
Scientific		publications	
journal			
Indicator 4 of	Cellulose Chem. Technol	2007	SJR 0.383, IF 1.3, Q2
Annex 5a		2016	SJR 0.330, IF 0.908, Q3
	Chemistry of Natural	2010	SJR 0.251, IF 0.8, Q3
	Compounds		
	J Univ Chem Technol Met	2013	SJR 0.146
	Oxidation communications	2011	SJR 0.211, IF 0.489, Q3
	Bulgarian Chemical	2017	SJR 0.156, IF 0.242, Q4
	Communications		
	SGEM2017, Conference	2017	ISBN 978-619-7408-29-
	Proceedings		4/ISSN 1314-2704, SJR
			0.212
	Journal of Environmental	2015	SJR 0.592, IF 0.81, Q3
	Protection and Ecology		
Indicator 7 of	J Univ Chem Technol Met	2011	
Annex 5a		2014	SJR 0.205
		2024	SJR 0.196
	Bulgarian Chemical	2018	SJR 0.137, IF 0.42, Q4
	Communications	2021	SJR 0.137, IF 0.39, Q4
	Compt. rend. Acad. bulg. Sci.	2015	SJR 0.209, IF 0.278, Q3
		2016	SJR 0.205, IF 0.321, Q3
	Int. J. Environ. Sci. Technol.	2016	SJR 0.592, IF 2.3, Q2
	Cellulose Chem. Technol	2018	SJR 0.277, IF 0.964, Q3
		2019-2	SJR 0.273, IF 1.073, Q3
		2023	SJR 0.257, IF 1.467, Q3
	Molecules	2023	SJR 0.704, IF 4.9, Q2
	ScienceRise: Pharmaceutical	2023	SJR 0.16, IF 0,82, Q3
	Science		

Arch. Metall. Mater.	2025-2	SJR 0.235, IF 0.7, Q3
Journal of International	2012	ISSN 1313-2339
Scientific Publications:		
Materials, Methods &		
Technologies		
Journal of International	2013	ISSN 1313-2339
Scientific Publications:		
Materials, Methods		
&Technologies		
Proceeding 9th International	2013-2	Web of Science, ISBN: 978-
Conference on		80-86238-58-6
Polysaccharides-		
Glycoscience		

My contributions are of a scientific and applied nature and can be grouped into the following thematic areas:

No.	Thematic area	Publications
1.	Preparation and characterization of low molecular	1, 2, 3, 4, 5, 6, 25
	weight phenolic compounds from lignocellulosic	
	materials with potential application as oxidation	
	inhibitors.	
2.	Characterization and investigation of the	7,8, 9, 10, 11, 18, 19, 20, 21, 22, 23,
	possibility of utilizing biomass waste products	24, 26, 27, 28
	(hydrolysis lignocellulosic materials, bark,	
	agricultural waste) as absorbents;	
3.	Characterization and utilization of waste and	13, 14, 15, 16, 17
	secondary industrial products.	

In thematic area 1 I declare 7 scientific publications in refereed and indexed journals.

Publications from [1] to [6] and [25] are an extension and upgrade of the research on the topic of my dissertation work.

The chemical processing of wood to cellulose and monosaccharides is associated with the conversion of about one ton of the raw material into lignocellulosic material as waste. In recent years, the production of bioethanol from plant raw materials has increased, generating such waste, currently having application only as an energy source. Due to the peculiarities of its chemical structure, lignin is a suitable raw material to produce monomeric phenolic compounds with an inhibitory effect on the oxidation of hydrocarbons.

Lignin is an amorphous three-dimensional natural polymer, the structure and reactivity of which depend on the method of isolation from the lignocellulosic matrix. The main monomeric units that make up lignin are p-coumaryl, coniferyl and sinapyl alcohol. Understanding their spatial conformation and their behavior in different solvents can provide important information for predicting the dimerization and polymerization processes occurring during the formation of the lignin macromolecule. In the publication [1] *S.Nenkova, V. Momchev, T. Vasileva, Structure prediction of alkaline activated hydrolysis lignin based on the study of its model compounds, Cellulose Chemistry and Technology, 41(1), 29-35, 2007*, computational chemistry methods were applied to the structure of alkaline activated hydrolysis lignin (AAHL) and its precursors (coniferyl and sinapyl alcohol) in order to predict the possibilities for chemical reaction. Conformations and spatial structures of the main monolignols and AAHL were obtained, calculated using the semi-empirical method MOPAC2002, as well as the molecular mechanics method MM2. The solvent effect was calculated again using MOPAC2002.

In the publication [2] <u>T. Radoykova</u>, S. Nenkova, K. Stanulov, Production of phenol compounds by alkaline treatment of poplar wood bark, Chemistry of Natural Compounds, 46(5), 807-808, 2010 (3 citations in Scopus) the possibility of obtaining low molecular weight phenolic compounds by alkaline treatment of poplar wood bark (waste material from the woodworking industry) was investigated. It was found that alkaline treatment is an effective process in which the main part of lignin is destroyed and as a result low molecular weight phenolic compounds are obtained. Alkaline treatment of the bark was carried out in stirred stainless steel autoclaves, in a polyethylene glycol bath at 180°C for 2, 4 and 6 hours. An aqueous solution of NaOH (3, 5 and 7%) was used as a depolymerizing solution at different bark/NaOH solution ratios – 1:6, 1:8 and

1:10. Using three-fold liquid-liquid extraction with toluene (ratio of extractant: aqueous phase - 1:5) from the aqueous phase the following compounds were isolated and identified by gas chromatography with mass spectrometry detector (GC/MS): 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, etc. The amounts of the obtained extracts, insoluble residue and precipitated and non-precipitated lignin were determined.

Publication [25] S. Nenkova, <u>T. Radoykova</u>, K. Stanulov, Preparation and antioxidant properties of biomass low molecular phenolic compounds, (Review), J Univ Chem Technol Met, 46 (2), 109-120, 2011 is a review article presenting the possibilities for obtaining valuable products with antioxidant properties from plant biomass. Many studies on the methods for the destruction of lignin to low molecular phenolic compounds and the use of the latter as antioxidants have been reviewed. The inhibitory effect of these compounds is of fundamental importance. Their application in stabilizing motor fuels, in the food industry and in medicine is of scientific and applied importance.

The oxidative stability of gasoline and lubricants is one of their most important operational properties. Additives are used to improve their chemical stability, with phenolic antioxidants being one of the most effective. In the article [3] *T. Radoykova*, *K. Stanulov*, *S. Nenkova*, *Lingin-derived methoxyphenols as antioxidant additives for gasoline, Oxidation communications, 34 (2), 463-468, 2011, (3 citations in Scopus)*, the possibility of using phenolic compounds obtained by alkaline destruction of poplar bark (2-methoxyphenol, 2.6-dimethoxyphenol, 3-hydroxy-4-methoxybenzaldehyde (vanillin) and 1-(4-hydroxy-3-methoxyphenyl) ethanone) as antioxidants was investigated. The induction period of gasoline containing different amounts (25, 75 and 200 ppm) of phenolic compounds was determined. It was shown that their effect was comparable to that of the most widely used low-temperature oxidation inhibitor – ionol. FT-IR spectra proved the antioxidant efficiency of the phenolic compounds isolated from the destruction of poplar bark.

For the first time in the publication [4] <u>T. Radoykova</u>, S.Nenkova, I. Valchev, Black liquor lignin products, isolation and characterization, J of Chem. Tech and Metallurgy, 48 (5), 2013, 524-529, (18 citations in Scopus) the nature of the compounds contained in the liquid phase separated after isolation of sulphate lignin from black liquor (residual solution from sulphate pulping of wood) by three-fold extraction with toluene (1:5 ratio organic: liquid phase), and subsequent two-fold extraction with ethyl acetate (1:5 ratio organic: liquid phase). The same extractions were used

to isolate the low-molecular components obtained during the destruction of sulphate lignin after its alkaline treatment at 180oC and a duration of 4 hours. By GC/MS analysis in both toluene extracts the following compounds were identified: 2-methoxyphenol, 2,6-dimethoxyphenol, 4hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3methoxyphenyl) 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone, ethanone. 4-ethyl-2methoxyphenol. The toluene extract of black liquor also contains 4-hydroxy-3-methoxyphenyl propanone; 1,2,4-trimethoxybenzene; 1,2 cyclohexane dicarboaldehyde, 1,3-cyclopentanedione 2,4-dimethyl. The main compounds extracted with ethyl acetate solvent are: 2,6-dimethoxyphenol; 2-methoxyphenol and 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone. as well as other ketones, aldehydes and acids that are not extracted in the toluene extract. It was found that the toluene and ethyl acetate extracts do not contain organically bound sulphur, which is essential for their potential application. Only octa atomic sulphur was identified in the toluene extract of black liquor.

A comparative kinetic analysis of the alkaline hydrolysis of two types of poplar biomass bark and wood chips - outlined the effect of the process duration and NaOH concentration on the yield of toluene extract during alkaline hydrolysis. [5] T. Radoykova, G. Radeva, S. Nenkova, Comparative kinetic analysis of poplar biomass alkaline hydrolysis, Cellulose Chem. Technol., 50(2), 269-274, 2016, (3 citations in Scopus.) Kinetic equations describing the kinetics of the process were verified. The values of the initial and current rates were calculated. The yield of low molecular weight phenolic compounds obtained from poplar bark is higher and the relative decrease in the rate during the process is smaller, despite the higher lignin content. A kinetic equation is proposed, valid for both types of poplar biomass. Under the established optimal conditions from previous studies, alkaline treatment of waste hydrolysed lignocellulosic materials from wheat straw after acid (130°C) and enzymatic hydrolysis was carried out; wheat straw after steam-explosion (190°C) and enzymatic hydrolysis; corn stalks after acid (130°C) and enzymatic hydrolysis; corn stalks after steam-explosion (190°C) and enzymatic hydrolysis; paulownia after steam-explosion (190°C) and enzymatic hydrolysis [6] <u>T. Hr. Radoykova</u>, S. K. Nenkova, I. V. Valchev, Monomeric phenolic compounds from hydrolysed waste lignocellulosic materials, Bulgarian Chemical Communications, 49(1), 40 - 45, 2017. By sequential extraction with two solvents, described in the article [4], NMPS were isolated from the destruction of lignin contained in the starting biomass. The main compounds identified by GC/MS in the toluene extract were: 2,6-dimethoxyphenol (from 13.7 to 46.4 area %); 1-(4-hydroxy-3,5-dimethoxyphenyl) ethanone (from 22.6 to 36.8 area %) and 2-methoxyphenol (from 11.6 to 24.2 area %). Other identified compounds are: 3-ethylphenol, 4-ethyl-2-methoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, etc. The total yield of extracted monomeric compounds after 6 hours of alkaline treatment is from 16.45% mass lignin (paulownia, after steam explosion treatment) to 18.50% mass lignin (straw, after steam explosion treatment, followed by enzymatic hydrolysis). It was found that the highest total yield of low molecular weight compounds from the waste is obtained with after steam explosion pretreatment.

The main contributions that could be distinguished in the presented scientific direction are:

- The possibility of obtaining valuable low-molecular phenolic compounds with antioxidant activity from various waste hydrolysed lignocellulosic materials (bark; technical hydrolysed lignin; sulphate lignin; agricultural waste from bioethanol production straw, corn cobs after various treatments) has been proven;
- For the first time, the behavior of lignin-derived compounds such as 2-methoxyphenol, 2,6-dimethoxyphenol, vanillin, 1-(4-hydroxy-3-methoxyphenyl) ethanone and others when added to hydrocarbons (liquid paraffin and automotive gasoline) has been studied.
- > For the first time, it has been established and proven that lignin-derived NMFS can be used as additives to increase the chemical stability of automotive gasoline.
- > The conditions for the extraction of these compounds from various waste biomasses have been optimized, which creates prerequisites for their industrial application.
- ➤ For the first time, the nature of the organic compounds from the liquid phase separated after the isolation of sulphate lignin from black liquor (residual solution from the sulphate digestion of wood) has been studied.
- > For the first time, the low-molecular products obtained from the alkaline treatment of technical hydrolysed lignin, used for its activation, have been studied.

In the publications of thematic area 2, various instrumental methods and techniques for the characterization of waste plant materials with practical application have been used. In this area, I declare 15 scientific publications, of which 3 are in proceedings of scientific conferences, presented in Conference Proceeding in Scopus and Web of Science and 2 are in Conference Proceeding with ISSN number.

To produce bioethanol from cellulosic biomass (production of second-generation bioethanol), a pretreatment process is used to open the structure of the cellulose component and support enzymatic reactions that break down cellulose to glucose. The efficiency of enzymatic hydrolysis depends mainly on the degree of opening of the cellulose chains in the previous processing stage. Acid hydrolysis and hydrothermal treatment remove the main part of the hemicelluloses, during which the accessibility of enzymatic macromolecules to the cellulose chains increases significantly. In the steam explosion method, the cell walls are further destroyed, which favours cellulose hydrolysis during the processing of the wood raw material. All these methods have one drawback - the lignocellulose complex remains practically unaffected. The efficiency of enzymatic hydrolysis will increase if the lignin, which blocks the cellulose chains, is removed. Classical delignification methods are not applicable in this case. The use of ethyl alcohol or other organic solvents has a positive effect, but these technologies have accompanying problems that make them inapplicable so far. The process must be highly selective and not lead to the destruction of the carbohydrate part. Peroxides can be used for partial depolymerization of the lignin-carbohydrate complex. The most selective agent is peracetic acid. The peroxide and peracetic acid treatment of agricultural lignocellulosic cellulose was investigated [27] S. Petrin, I. Valchev, T. Radoykova, S. Nenkova, Application of peroxides for bioethanol production from lignocellulosic materials, Proceeding 9th International Conference on Polysaccharides-Glycoscience, 06 - 08 November 2013, Prague, Czech Republic, p. 178-180, 2013. (Web of Science ISBN: 978-80-86238-58-6). The process was carried out after hydrothermal and before enzymatic hydrolysis. The glucose and furfural content were determined using a Dionex HPLC system. An increased glucose yield was found, proving that peroxides are suitable and effective agents for bioethanol production.

In the production of sugars for second-generation bioethanol, the main problem is the utilization of waste hydrolysed lignin, containing a certain number of difficult-to-hydrolyse

polysaccharides. The sorption properties of hydrolysed lignins have been proven in many publications. These materials are effective alone or in combination with other materials for the purification of aqueous solutions from heavy metal ions (Pb, Cu, Zn and Cd and Ni(II) ions). In this regard, it was of interest to evaluate the possibility of utilizing various waste lignocellulosic materials as absorbents of heavy metal ions and to study the mechanism of absorption.

The adsorption of Mn²⁺ ions by samples of hydrolysed lignocellulosic materials (HL) and alkaline-treated hydrolysed lignin (AAHL) obtained from paulownia, wheat straw and corn stalks was investigated in the article [8] *T. Hr. Radoykova*, *S. V. Dimitrova*, *K. I. Aleksieva*, *S. K. Nenkova*, *I. V. Valchev*, *D. R. Mehandjiev*, *Comparative Mn²⁺ adsorption on waste lignocellulosic materials*, *Journal of Environmental Protection and Ecology 16 (1)*, 23–32, 2015, (9 citations in Scopus) by IR spectroscopy and EPR analysis. Nitrogen adsorption isotherms were used to calculate the specific surface area using the BET (low-temperature nitrogen adsorption (Brunauer–Emmett–Teller)) equation. It was found that the adsorption isotherms of Mn²⁺ ions on the studied materials are of the Langmuir type. Their EPR spectra after manganese adsorption consist of six hyperfine splitting lines specific for Mn²⁺ ions, which are in such a way that there is no interaction between them.

The adsorption properties of lignocellulosic by-products from bioethanol production (Populus alba L. (Poplar) and Robinia pseudoacacia L. (White Acacia)) towards silver ions (Ag+) were investigated in publications [9] *P. S. Vassileva, T. Hr. Radoykova, A. K. Detcheva, I. A. Avramova, K. I. Aleksieva, S. K. Nenkova, I. V. Valchev & D. R. Mehandjiev, Adsorption of Ag+ ions on hydrolyzed lignocellulosic materials based on willow,paulownia, wheat straw and maize stalks, Int. J. Environ. Sci. Technol. 13(5), 1319–1328, 2016, (34 citations in Scopus)* and [10] *P. S. Vassileva, A. K. Detcheva, T. Hr. Radoykova, I. A. Avramova, K. I. Aleksieva, S. K. Nenkova, I. V. Valchev and D. R. Mehandjiev, Studies on Ag+ Adsorption Using Two New Lignocellulosic Materials Based On Populus Alba L. And Robinia Pseudoacacia L., Cellulose Chem. Technol., 52(7-8), 633-643, 2018, (9 citations in Scopus)*. The composition of the studied materials was determined by a series of chemical analyses. The texture parameters were calculated using low-temperature nitrogen adsorption-desorption isotherms. The adsorption mechanism was studied using IR, SEM, EPR and XPS spectroscopy. It was found that the adsorption is significantly affected by the pH value of the metal ion solution. The optimal pH value is in the range of about 4-5. The adsorption equilibrium is established within 5 minutes. The obtained XPS and EPR results

confirmed that the adsorption of Ag^+ ions on the studied waste materials goes through several stages. The last stage is the formation of a metal cluster Ag^0 . Both types of isotherms - Langmuir and Freundlich - can be used to describe the adsorption process.

XPS and IR spectrometry methods are effective for clarifying in depth the chemical composition of the studied materials and the nature of the functional groups on their surface. The surface concentration and the presence or absence of some functional groups was investigated by the XPS method in the publication [11] I. A. Avramova, T. Hr. Radovkova, I. V. Valchev, D. R. Mehandjiev, X-ray photoelectron spectroscopy investigations of lignocellulosic materials, Bulgarian Chemical Communications, 50 (3), 411 - 416, 2018, (1 citation in Scopus). The calculated O/C ratio confirmed the data from chemical composition methods that the surface of the paulownia and willow samples contains more lignin, while the surface of the straw sample contains more cellulose. Our studies showed that these materials can be used both as adsorbents for Ag+ ions and for obtaining silver-modified materials with antimicrobial properties. This idea was further developed in the publication [12] T. Hr. Radovkova, T. G. Angelova, P. S. Vassileva, N. V. Georgieva, A. K. Detcheva, K. I. Aleksieva, I. V. Valchev, S. K. Nenkova and D. R. Mehandjiev, Investigation Of Antibacterial Activity Of Waste Lignocellulosic Materials Doped With Silver, Cellulose Chem. Technol., 53 (5-6), 427-433, 201, (4 citations in Scopus). It was found that lignocellulosic waste materials obtained after enzymatic hydrolysis of plant raw materials with adsorbed silver have a high effect in the destruction of harmful bacteria, such as gram-positive Bacillus subtilis strain 3563 and gram-negative Escherichia coli K12 in aqueous solutions. The well-developed internal surface and the presence of oxygen-containing functional groups that adsorb silver ions are the basis of this activity.

In Bulgaria, the most promising agricultural raw materials to produce sugars for bioethanol are straw and corn stalks, as they achieve the highest sugar yield. The research in publication [26] *T. Hr. Radoykova, S. V. Dimitrova, K. I. Aleksieva, S. K. Nenkova, I. V. Valchev, D. R. Mehandjiev, Adsorption properties of waste lignocellulosic materials produced in reprocessing of wheat straw and maize stalks biomass, 15th International Symposium Materials, Methods & Technologies (MMT), June 10 – 14, 2013, Sunny Beach, Bulgaria, Journal of International Scientific Publications: Materials, Methods & Technologies, 7 (2), 190-201, 2013 were aimed at studying the adsorption properties of hydrolysed lignin (HL) from acid and subsequent enzymatic hydrolysis*

of wheat straw HL(s) and maize stalks HL(m) and of lignin obtained from them after alkaline treatment (alkaline activated hydrolysed lignin (AAHL) of Cu2+ ions from aqueous solutions.

The mechanism of adsorption, the role of the functional groups of the components of lignocellulosic materials such as adsorption centres, specific surface area was evaluated by IR spectroscopy, EPR and TG-DSC analyses. Nitrogen adsorption-desorption isotherms were used to calculate the specific surface area using the BET equation. It was found that the adsorption isotherm of Cu2+ ions on the studied samples is of the Langmuir type, with the parameters in the Langmuir equation depending on the starting material and the respective treatment. EPR spectra show that Cu2+ ions orient themselves towards oxygen ions and form a tetrahedral complex. Under the experimental conditions, sample HL(m) shows the best adsorption capacity for 1 g of sample. However, the maximum adsorption coefficient per unit surface area for the samples activated by alkaline treatment is higher than that for samples without such treatment.

It is known that during pyrolysis lignin depolymerizes to phenyl, guaiacyl and syringyl derivatives. These products can be used as fuel, as compounds for chemical synthesis or to produce phenolic resins. The biocoke obtained as a residue after pyrolysis can be used as fuel or can be processed into activated carbon with a wide range of applications. for the use of this method.

By chemical analysis, Py-GC-MS, DSC and calorific value determination, waste hydrolysed lignocellulosic materials from monosaccharide production were evaluated as energy raw materials. Analytical pyrolysis – Py-GC-MS/FID provides a rapid analysis of the composition of hydrolysed lignocellulosic materials. More than 200 chemical compounds were identified by Py-GC-MS analysis of the studied materials. The results showed [28] *T. Radoykova*, *T. Dizhbite*, *G.Dobele*, *S. Nenkova*, *I. Valchev*, *Characterization of hydrolysed lignocellulosic materials for energy utilization*, *Proceeding 9th International Conference on Polysaccharides-Glycoscience*, 06 - 08 November 2013, Prague, Czech Republic, p. 200-204, that most of the degradation products are aldehydes, ketones, sugars and products derived from carbohydrates. The obtained results for calorific values of these materials are between 21.02 and 23.37 MJ/kg, proving the possibility of their application as alternative fuels.

Of the biomasses studied, technical hydrolysed lignin has the highest calorific value, probably due to its higher lignin content. Thermogravimetric analysis revealed that the hydrolysed materials from agricultural crops (HL(m) and HL(s)) decompose in three, relatively simple steps. Industrially produced technical hydrolysed lignin (THL) showed a complex decomposition

process resulting from at least 5 overlapping steps with the main maximum of the mass loss rate at 377.8 °C. Instead of a single peak at 300 °C, THL showed a complex destruction process in the temperature range 270 - 310 °C.

In the article [18] D. Ch. Vladov, L. P. Raicheva, R. N. Nikolov, <u>T. Hr. Radoykova</u> and S. K. Nenkova, Preparation Of Efficient Carbonaceous Material (Active Carbon) From Hydrolysed Lignin Through Direct Activation With Phosphoric Acid, Cellulose Chem. Technol., 53 (7-8), 731-738, 2019, (4 citations in Scopus) the possibility of obtaining an effective carbon material (activated carbon) from technical hydrolysed lignin by chemical activation with H₃PO₄ was investigated. Micro-mesoporous carbon samples were obtained, possessing very good adsorption-textural parameters: specific surface area ranging from 1029 to 1824 m²/g, micropore volume from about 0.320 to 0.500 m³/g, as well as mesopore volume varying within wide limits, depending on the preparation conditions. The highest surface specificity is possessed by the sample treated with H3PO4 in a ratio of 1:5. The largest micropore volume was shown by the sample treated with H3PO4 in a ratio of 1:1.

Activated carbon was obtained from hydrolysed lignocellulosic biomass after chemical activation with potassium hydroxide and phosphoric acid [19] *V. Toteva, T. Radoykova, Ch. Tzvetkova, L. Raicheva, S. Nenkova, R. Nickolov, Application of waste-derived activated carbon as a sorbent for Re ions recovery from acidic aqueous solution, Bulgarian Chemical Communications, 53 (3), 287 – 293, 2021, (1 citation in Scopus)*. The texture parameters of the obtained adsorbents were determined by low-temperature nitrogen adsorption; their thermal stability was studied by DTA/TG, and the surface functional groups - by FTIR spectroscopy. The adsorption properties of the obtained activated carbon towards perrhenate ions from aqueous solution were studied at three different pH values. It was found that the adsorbent obtained after activation of hydrolysed lignin with KOH has a significantly better adsorption capacity than that obtained after activation with H₃PO₄. The maximum adsorption value of the perrhenate anion – 95.7% was obtained at a rhenium concentration in the solution of 5 mg L⁻¹ and pH 2. The results of this study showed that the obtained activated carbon can act as an effective adsorbent for perrhenate ions from acidic wastewater.

In the study [20] I. Naydenova, <u>T. Radoykova</u>, T. Petrova, O.Sandov, I.Valchev, Utilization Perspectives of Lignin Biochar from Industrial Biomass Residue. Molecules 2023, 28(12), (12 citations in Scopus) technical hydrolysed lignin (THL) was carbonized in a horizontal tube furnace

at atmospheric pressure, in an inert atmosphere and at three different temperatures (500, 600 and 700°C). The thermal stability (thermogravimetric analysis) and textural properties of the resulting biocoke were investigated. The surface area and pore volume were determined by low-temperature nitrogen absorption (Brunauer–Emmett–Teller (BET)). Infrared spectra (FTIR) of the resulting biocoke showed that with increasing carbonization temperature, the functional groups were reduced, forming a material with polycyclic aromatic structures and a high percentage of condensation. The biocoke obtained at 600 and 700°C possesses properties characteristic of microporous adsorbents.

In the publication [21] A. Mechshanova, V. Polyakov, T. Radoykova, The study of the natural substances obtained from the poplar buds and their use for protection against the action of ionizing radiation, ScienceRise: Pharmaceutical Science 3(43)2023 the possibility of identifying and quantifying flavonoids by UV-VIS spectrometry and HPLC/MS method in the extract of poplar buds is shown. The main components identified in the poplar bud extract are: 2',6'-dihydroxy-4-methoxychalcone – 2.33%, 3,4-dihydro-2',6'-dihydroxy-4'-methoxychalcone – 2.33%, pinobaxin – 1.91%, chrysin – 0.76% pinostrobin – 0.04%, pinocembrin – 0.61%, tectochrysin – 0.54% and galangin – 0.18% dry matter. The results showed a significant radioprotective effect on low intensity ionizing radiation. The penetrating radiation decreased from 78% at a layer of 0.5 mm to 10% at a layer thickness of 3 mm. The subsequent increase in the thickness of the protective layer (>3 mm) had no effect on the radiation strength.

In recent years, new methods and technologies for growing individual crops have been persistently sought in order to increase their productivity and improve the quality of production. In Publication [22] Anna Mechshanova, Vladilen Polyakov, Temenuzhka Radoykova, Obtaining Balsamic Poplar Bud Essential Oil by The Barothermal Method and Studying the Effect of its Aqueous Emulsions on Seed Germination and Growth of Tomato Plants, Cellulose Chem. Technol., 57 (9-10), 953-962, 2023 essential oil was obtained from poplar buds by the barothermal method and the effect of an aqueous emulsion of poplar oil on the growth and development of tomato seeds was studied. The poplar essential oil obtained under optimal conditions was standardized by organoleptic and physicochemical indicators. It was found that the use of an aqueous emulsion of the oil has a significant impact on the morphogenesis, physiological and biochemical parameters of tomato seeds.

In Publication [23] Mechshanova A., Polyakov V., Surleva A., Radoykova T., Obtaining of balsamic poplar extract as biostimulant for agricultural plants, Journal of Chemical Technology and Metallurgy, 59, 2, 2024, 269-278 the qualitative and quantitative composition of extracts obtained from waste from the timber industry from poplar wood (buds, leaves, twigs) was determined. It was proved that the use of poplar extract has a significant impact on the morphogenesis, physiological and biochemical indicators and productivity of white cabbage variety Podarok. Thus, in plants grown from seeds soaked with 0.03% aqueous emulsion of the extract, the respiration coefficient is 2.7 mg CO₂ per 1 g of dry matter, which is 540% compared to control 1 (C1), and compared to control 2 (C2) - 270% and a higher yield compared to other treatment options. The intensity of respiration and productivity of plants that received foliar feeding with 0.003% aqueous emulsion of the extract also exceeds the corresponding indicators in the control samples. Thus, the intensity of respiration in the initial phase of growth of the rosette and roots is 1.9 mg CO2 per 1 g of dry matter, which is 380% compared to control 1 (C1) and 190% compared to control 2 (C2). The yield is 1008 c/ha.

The preparation and characterization of new nanocomposite wood fibrous materials modified with copper sulfide was followed in a scientific work [24] S. K. Nenkova, M. M. Dragnevska, S. D. Lekova, S. B. Parvanov, T. Hr. Radoikova, Nanocomposite wood fibrous materials for electromagnetic wave protection, 14th International Symposium Materials, Methods & Technologies (MMT), June 11 - 15, 2012, Sunny Beach, Bulgaria, Journal of International Scientific Publications: Materials, Methods & Technologies, 6(2), 370-380, 2012. It was found that these materials have a high physicomechanical index and improved electrical conductivity and can be used for electromagnetic protection. In the scientific work [7] <u>T. Radovkova</u>, S. Nenkova, N. Georgieva, D. Todorova, T. Angelova, Improvement of operational properties of wood materials by modification throught the penetration, 17th International Multidisciplinary Scientific GeoConference SGEM 2017, SGEM2017 Vienna GREEN Conference Proceedings, ISBN 978-619-7408-29-4 / ISSN 1314-2704, 27 - 29 November, 2017, Vol. 17, Issue 63, 579-586. the possibility of preserving wood by modification by the method of impregnation with various agents and the study of the impact of the process on some operational properties of the wood material was investigated. The experiments were conducted with poplar wood, which has a low density with a well-developed capillary system, good absorption capacity and belongs to the low operational capacity wood species. Alkaline-activated hydrolysed lignin (AAHL), Cu₂S and maleic anhydride (MA) were used to modify poplar wood. The modification was carried out by the hot and cold immersion method. The modified samples were characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric methods (DTG, TG), water absorption and antibacterial activity against Bacillus subtilis (G+) and Escherichia coli K12 (G-) was determined. The IR spectra of the modified samples showed changes in the structure of the wood samples because of physical and chemical processes. The DTG and TG methods were used to monitor the change in the weight of the samples as a function of temperature. Comparing the weight loss of three types of modified wood samples, it was found that the used AAHL and Cu₂S agents have a positive effect on thermal stability, having a retarding effect. The obtained results show that the samples modified with maleic anhydride and Cu₂S are characterized by reduced water absorption. It was found that the studied modified wood samples exhibited antibacterial activity against Escherichia coli K12. The best antibacterial effect was observed in a sample modified with maleic anhydride.

The main contributions related to my research in the second scientific direction can be summarized as follows:

- ➤ Possibilities for utilization of various hydrolytic lignocellulosic materials as adsorbents of heavy metals (Mn²+, Cu²+, Ag+) have been studied, the mechanisms have been investigated, adsorption isotherms and their textural parameters have been determined.
- > It has been shown that waste lignocellulosic materials modified with silver have antimicrobial properties against pathogenic microorganisms.
- Various waste lignocellulosic materials have been evaluated as energy raw materials, with proven high calorific value and potential for application as fuel.
- > Methods have been developed for obtaining activated carbon from hydrolytic lignin with excellent textural characteristics and high adsorption capacity for heavy and rare metals.

The third scientific direction brings together 5 publications focused on the utilization of waste (tail) and by-products (blast furnace slag) from metallurgy and from thermal power plants (fly ash) with the aim of their utilization, solving important environmental problems.

In publication [13] *I.Mihailova*, *T.Radoykova*, *G.Ivanov*, *D.Stoyanova*, *D.Mehandjiev*, *Slag-based materials as catalysts in oxidation reactions*, *J Chem Technol Met*, *49*(4), *391-401*, *2014*. The possibility of creating new active catalysts for waste gas purification by complete oxidation of carbon monoxide and organic compounds obtained from metallurgical slag was investigated. The synthesis of catalysts is carried out by acid and thermal activation of metallurgical slag, in which, in addition to increasing the catalytic activity, the specific surface area also increases several times. Several modern instrumental techniques (ICP-OES analysis, Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TGA), X-ray Diffraction Analysis (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) were used to study the composition and structure of the obtained materials, as well as the phase formation processes. The textural properties and chemical composition of the surface were investigated by scanning electron microscopy (SEM), low-temperature nitrogen absorption (BET analysis) and X-ray photoelectron spectroscopy (XPS).

The effect of the processing of granular blast furnace slag in an autoclave on its catalytic activity with respect to CO oxidation was studied in publication [14] *I. K. Mihailova*, <u>T. H. Radoykova</u>, G. M. Ivanov, P. V. Vassileva, D. R. Mehandjiev, Blast furnace slag-based materials for catalytic applications, Compt. rend. Acad. bulg. Sci., 68 (5), 595–600, 2015. The results showed that autoclaving after chemical treatment of the slag with nitric acid or nitric acid and ammonia, leads to an increase in the specific surface area, but reduces the concentration of catalytically active complexes (CAC) on the catalyst surface. The latter effect is due to leaching of catalytically active elements in the slag during autoclaving.

By modifying blast furnace slag, materials with a high specific surface area (329–621 m2g-1) were synthesized [15] *I. K. Mihailova*, *T. H. Radoykova*, *D. R. Mehandjiev*, *Synthesis of Materials with A High Specific Surface Area from Blast Furnace Slag, Compt. rend. Acad. bulg. Sci. 69 (4), 431–438, 2016. The process includes chemical and thermal treatment. During the chemical treatment, four samples obtained at different values of pH. The relationship between the synthesis conditions, the chemical composition and the structure of the obtained materials was established. Several modern analytical methods (ICP-OES, XRD, FTIR, SEM, low-temperature nitrogen absorption (BET analysis) and other methods were applied for phase and structural characterization of the materials. The chemical composition and structure of the materials, including their specific surface area, was significantly changed from that of the starting blast*

furnace slag. It was found that in the synthesized materials the predominant phase was an amorphous silicate or aluminosilicate phase with less than 6% barite. The possibility of using the newly synthesized materials as catalysts or catalyst supports was proven.

Reusing industrial waste or by-products as raw materials can solve important environmental problems. Articles [16] Radoykova T., Surleva A., Ilieva D., Angelova L., Chernev G., Characterization of mine tailings and fly ash from Bulgaria as raw materials for geopolymerisation, has been finally accepted for publication in Archives of Metallurgy and Materials, (2025), 70(1), pp. 445–452 and [17] **Radoykova T.**, Surleva A., Ilieva D., Angelova L., Testing of geopolymer raw materials: Validation of methods and practical aspects, Arch. Metall. Mater. 70 (2025), 1, 165-169. They are focused on geopolymers. They are a modern alternative to traditional construction materials with a low CO₂ footprint. The chemical and mineralogical composition of the raw materials is of crucial importance for the structure and physical properties of geopolymers. The potential application of mine waste and coal combustion by-products from Bulgaria as raw materials to produce geopolymers was assessed [16]. Samples from mine tailings and coal combustion by-products from thermal power plants were characterized by determining the chemical and mineralogical composition, granulometric composition, physicochemical parameters of the aqueous suspension. The content of heavy metals was determined by ICP-OES after acid treatment with aqua regia. Appropriate validated analytical methods were combined to extract detailed information. The validated procedures [17] were applied to mine waste and coal combustion by-products from Bulgaria, Romania and Portugal. The results show that the investigated raw materials can be used as geopolymer precursors.

The main contributions in the latter scientific direction can be summarized as follows:

- > The possibility of obtaining catalysts from metallurgical slag for waste gas purification has been demonstrated.
- > Mining waste (tailings) and fly ash (from coal-fired power plants) have been characterized as raw materials to produce geopolymers.
- > Methods for the analysis of these precursors for geopolymers have been validated.