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for the scientific contributions of assist. Prof. PhD. eng. Metodi Kirilov Mladenov,

submitted for participation in a competition for "associate professor" in scientific specialty 5.10. Chemical technologies (Influence of the ecological factors on the man and his protection from the harmful ecological factors), announced by the University of Chemical Technology and Metallurgy with publication in the state gazette, issue 108 from 22.12.2020.

The current scientific contributions report was made on the basis of 27 publications submitted for participation in the competition for the academic position of "associate Professor", 13 of which are in scientific journals indexed and referenced in world databases (with awarded IF and/or SJR), and 14 are in scientific journals with reviewers or in edited collective volumes. In addition, a total of 54 citations of the entire candidate's works have been noticed so far. According to the publicly available information in the Scopus database, the Hirsch index (h-index) is 3 (excluding auto-citations). The total number of participations in scientific forums and conferences is 36, of which 28 poster papers and 2 e-posters.

The main results and scientific contributions are summarized in the following scientific areas:

1.   *Characterization of materials, waste and soils, in terms of environmental factors and alternative material and energy sources. Modeling and simulations.*

2.   *Registration, analysis and control of pollutants and toxic substances affecting living organisms and humans.*

3.   *Ecological and social factors, healthy and safe working conditions.*

The components of the environment are considered as a kind of environmental factors influencing the biological processes and transformations of

matter and energy along the food chain and ultimately on man. Environmental factors are directly related to human life and activity, including in production and processing enterprises, as well as to the requirements for ensuring occupational safety and health (OSH), a clean environment and sustainable economic development. The done scientific work is mainly in the field of research of various substances, mixtures, soils and wastes, the results of which are presented in the applied scientific publications. Their composition and properties were characterized with a view to their definition as ecological factors, having a direct and/or indirect impact on the environment and man. The studied objects are diverse, both in terms of the source of their generation and in terms of their composition and properties. The studies were performed using a variety of analytical methods and procedures – "classical" chemical analysis, DTA/DSC (differential thermal analysis/differential scanning calorimetry), WD-XRF (wave-dispersive X-ray fluorescence analysis), TXRF (total X-ray fluorescence analysis), ICP-OES (inductively coupled plasma with optical emission spectrometry), ICP-MS (inductively coupled plasma with mass spectrometry), FAAS (flame atomic absorption spectrometry), AES (atomic emission spectrometry), GC/MS (gas chromatography with mass spectrometry), GC-ECD (gas chromatography in combination with electron capture detector), UV-VIS (spectrophotometry in the visible and ultraviolet range), biosensors, etc. A pot tests experiments were also conducted to test the agro-ecological efficiency of various substances and mixtures, in order to verify the possibilities for improving the soil composition and properties and to establish the impact of the available hazards on components and parameters of the environment and man.

Scientific area 1. *Characterization of materials, waste and soils, in terms of environmental factors and alternative material and energy sources. Modeling and simulations.*

Utilization of waste as a secondary material and energy resource is a challenge for many researchers and a topical issue. In this regard, the composition of composite mixtures based on waste ash from wood biomass, green lye and sulfuric acid were modeled. They were analyzed by differential thermal analysis and

thermogravimetry (DTA/TG). The thermal stability of the obtained products and the enthalpy changes at temperatures from 20 to 1000 °C were established. A chemical mechanism of the ongoing interactions has been proposed, and it has been found that the model mixtures are thermally stable at the temperatures of traditionally used soil improvers and can find practical application [I.3].

Studies have been carried out with three different types of compost obtained by different composting methods [I.8]. The composition of these types of compost has been established – the contents of nutrients and some microelements and heavy metals have been studied. Physicochemical parameters pH, conductivity, bulk density, porosity and loss of ignition (LOI), are also determined. The changes of the physical, chemical and biological parameters of the process of "home" composting of two main categories of bio-waste: "greens" and "browns" were studied in order to establish their impact on the process [III.8, III.10]. The change of the content of the main nutrients (K, N, P) and C was observed and the carbon/nitrogen ratios were determined during the composting process. The appearance and development of various living organisms in the compost mass were monitored during the active phase of the process [III.10].

Through tests for the agro-ecological efficiency of various mixtures, the possibility for improving the properties of two types of soils was tested. For this purpose, a series of mixtures with different ratios of the initial components used in them were modeled and prepared. It has been found that compost additives have the most significant effect on acidity (pH), porosity and carbon content. There are also proportional dependences of the change in the content of total and soluble forms of phosphorus, depending on the amount of compost used [I.5].

The content of carbon and nutrients in real soils was studied by adding waste, composts and products prepared on the basis of waste substances. An analysis of the content of nutrients and toxic substances was performed and recommended addition rates were determined in order to achieve a positive effect on soil properties. The results of the studies with green peas (*Pisum sativum*) and pepper (*Sweet pepper*) confirm the possibility of increasing the content of carbon and nutrients in the tested soils [III.4].

Soils, as an ecological factor, have an impact on wetlands and on the vital activity of the waterfowl inhabiting them. The condition of the soils in the Srebarna National Nature Reserve has been studied. Regarding the protection of waterfowl migrating birds, the reserve is of cross-border importance, which is why the study is concentrated on seven soil samples, representative of the entire territory of the reserve. In the samples, the parameters acidity (pH), electrical conductivity, nutrient content and the presence of heavy metals, were analyzed. The results of the study show that the soils in the area have a relatively good stock in terms of carbon (humus), Ca, Mg, K and P. Despite the presence of some heavy metals and metalloids, it was found that their concentrations are below the normative values [I.7].

In 2006 for the first time an analysis of soils contaminated with heavy metals from the area of the metallurgical plant "Eliseina" JSC, station Eliseina was performed by applying the technique of wave-dispersive X-ray fluorescence analysis [I.1, I.2]. Soil samples taken near the source of pollution (factory chimney) and at a distance of up to 5 km were examined. The method of standard curve was used for the quantification of the analyzed elements. For this purpose, the matrix composition was modeled and the secondary standards samples with characteristics of natural soil were prepared [I.2]. Based on the obtained results, the pollutants present in the soils were identified: Cu, As, Pb and Cr [I.1, I.2]. In 2013, soil sampling were again carried out in the area, repeating the places of initial sampling and monitoring the changes in the composition and properties of soils in order to clarify their role as an environmental factor for nature and the population nearby. Processes of neutralization of soil acidity, reduction of the concentration of soluble forms of heavy metals and favorable processes of restoration of the permanent vegetation cover in the region have been established. The conducted field researches and visual observations showed the presence of the following plant species: cornelian cherry (*Cornus mas*), dog rose (*Rosa canina*), common horsetail (*Equisetum arvense*), silver birch (*Betula pendula*) and thorn trees (*Robinia pseudoacacia*)) [III.3].

In a subsequent study [I.6], eight soil samples from different areas in the Republic of Bulgaria and three types of meat used for human consumption were analyzed for the presence of pesticides: dichlorodiphenyl-dichloroethane (DDD);

hexachlorocyclohexane (HCH); hexachlorobenzene (HCB); dichlorodiphenyl trichloroethane (DDT) and its metabolite dichlorodiphenyldichloroethylene (DDE). Each of them poses a danger due to their ability to bioaccumulate and store up on the food chain and their subsequent entry into the human body. Due to the widespread use of organochlorine pesticides in the past, significant amounts of them are still found in nature, mainly in the form of by-products, which, however, often pose a more serious hazard than the primary product used. The results of the study identified the presence of the above pesticides in both the soil samples and the animal products, and the established concentrations are below the permissible normative values.

A mushroom (*Pleurotus ostreatus*) were cultivated on solid substrates from various organic wastes and composts. The formed mycelar blocks were placed in the environment of modeled soil mixtures containing contaminated soil from a non-ferrous metal mine. The period of adaptation and the formation of sporophores (fruiting bodies) were monitored [III.6, III.9]. It has been established that the metals Cu, Zn, Ni, Al, Bi, Mn and Fe are absorbed as a priority [III.6]. The degradation of phenol by tyrosinase isolated and purified from fungal mycelium developed on organic waste and composts were observed [III.9]. The dense homogeneous blocks formed between the micelle and the substrate can be used for the recovery of solid waste products and for direct application on contaminated soils, which is a promising method for bioremediation [III.6, III.9].

The simulation of natural processes and the creation of adequate mathematical models, which on the one hand to reflect their nature, and on the other hand to give a forecast for their development, is an extremely difficult task. Usually the created mathematical models are valid for a specific area of the process or under certain boundary conditions. Modeling and simulation of natural soil processes is significantly more complex than all other components of the environment. The complexity is determined by the natural connection of the chemical, physical and biochemical processes taking place in the soil. Study [III.2] presents the result of simulations of the process of fluid flow through a porous medium, the boundary conditions of which correspond to the parameters of a natural soil system, using a modeling and simulation program ANSYS Workbench CFX. The

initially established model can be used as a basis for subsequent refinement and establishment of the specific parameters of the porous body, which fully correspond to those characteristic of a real soil system.

Based on the accumulated experimental experience, a review of the system for ecological monitoring of soils in the Republic of Bulgaria and the monitoring schemes applied on the territory of the country was performed. The three levels of the monitoring system of the lands from the agricultural fund are analyzed, together with their personal schemes, regulating the points (landfills) for sampling, the parameters that are monitored and the periodicity of monitoring. The interrelations between the Bulgarian system and the European soil monitoring system are also considered. The paper also touches upon the issue of the necessary connection of the system with the regulated norms of the national legislation and the requirements imposed by the Bulgarian state standards regarding the equipment and the used devices [III.12].

Determining the composition of different types of waste, many of which have no analogue in the past, is crucial for deciding on their treatment. The accuracy of the result, in turn, helps to choose a specific method by which the relevant type of waste could be analyzed in a minimum of a short period of time. A study was performed on the applicability of the WD-XRF and TXRF techniques in characterizing biomass ashes, and the preliminary results obtained from the two methods were compared with the results of a third independent analytical method – FAAS [III.5]. In a separate study, modeling of the composition of standard secondary samples for "rapid" quantitative analysis of real molybdenum concentrate samples was performed using the technique of wave-dispersive X-ray fluorescence analysis [II.2]. For the preparation of the secondary standard samples, a molding matrix was designed and manufactured and glassy standard samples were cast, which were subsequently applied in the production process of a metallurgical plant.

By means of differential thermal analysis, new products for application in construction were investigated in order to establish the transition from solid to semi-liquid and liquid state (glass transition temperature). The studied products are based on a combination of two main components, the mixing of which activates their binding properties. Based on the obtained results, the thermal stability and the

beginning of thermal deformation of the mixtures, which are necessary for their practical application, have been established [II.1].

The waste olive meal was characterized in terms of chemical composition and the contained macro elements (N, P, K, Ca, Mg, C) and some microelements and heavy metals were determined (Al, Co, Cu, Fe, Zn, Ni , Cd, Mn, Mo, Pb, Cr, As, Se, and Sr) using spectroscopic methods such as FAAS, ISP-MS and ATR-FTIR (attenuated total reflection Fourier transform infrared spectroscopy). The main physicochemical parameters were also determined: (moisture and volatile compounds, raw oil, raw fibre, raw protein, ash residue and insoluble ash) [I.9]. In practice, the direction related to the application of meal as a material resource in animal husbandry is known. At the same time, there are alternative areas related to other economic sectors such as composting, biodiesel production, heat treatment and others, whose economic efficiency is still not sufficiently substantiated. Based on the results obtained for the composition, a follow-up study [I.10] examined the possibilities for exploiting the energy potential of meal and the prospects for creating "green" jobs.

An analysis and assessment of the pulp production in "Svilosa" JSC, Svishtov, was performed with regard to the types of waste generated during the preparation and processing of wood. The best available techniques (BAT) of sulphate pulp production plants are considered. Recommendations have been made for the implementation of modern methods and technological solutions in order to improve the ecological, technical and economic indicators of the existing productions in the complex "Svilosa" [III.1].

Scientific area 2. *Registration, analysis and control of pollutants and toxic substances affecting living organisms and humans.*

Biosensor techniques and chromatographic methods can be complementary in the primary screening of contaminants with hazardous substances and metabolites in different samples. Bioanalytical methods developed for the analysis of toxic substances provide fast and reliable real-time data by having a wide range of applications for testing exposure to toxic substances. They can be used to detect

many substances, including organic and inorganic compounds, bacterial toxins, mycotoxins, hormones, pesticides and heavy metals, which are often present as traces in the work environment and nature and have serious effects on humans. The current trend of approximation of the requirements set in the standards concerning safety management systems and environmental management systems determines the applicability of biosensors for environmental monitoring and in the assessment of exposure at the workplace. It is also necessary to continuously improve the operating parameters of biosensors, and for this purpose new carriers for immobilization continue to be synthesized and to isolate and study various enzymes from various sources. The main objective is to extend the lifetime of biosensors and to expand their ability to identify different substances and their application in different environments [III.14]. In support of the above, biosensors applicable to monitoring exposure to chemical and biological agents are considered in [III.13].

Waters is one of the environmental factors that have a direct impact on humans. Monitoring of spring waters and surface water flows from the area of the village of Bov was performed, characterized depending on their use (drinking or household needs) and after discharge of wastewater in them. In three sampling campaigns, in different climatic seasons, in periods before and after precipitation, monitoring was performed in order to determine the influence of rainwater on the composition and concentration of the analyzed elements in the studied samples. The obtained results are considered in the aspect of European Water Frame Directive and Drinking Water Directive. A number of chemical elements (Al, As, Ba, Cd, Cr, Co, Cu, Fe, Hg, Mn, Ni, Pb, Se, U, V, Zn and lanthanides) and physicochemical parameters (pH, conductivity, water hardness, chemical oxygen demand (COD_{KMnO4}); biological oxygen demand (BOD_5); dissolved oxygen; dissolved solids; suspended matter; dry residue; chlorides; sulphates; nitrates; phosphates) were analyzed. The possible influences of the performed mining activity in the region on the quality of the studied water sources are also considered [I.4].

Scientific area 3. *Ecological and social factors, healthy and safe working conditions.*

A new direction related to "green" jobs has undergone active development in recent years [III.11, I.10]. The term "green" jobs means those that contribute to the protection of the environment by protecting ecosystems and biodiversity, reducing the consumption of energy and raw materials, reducing waste and generated pollutants in the environment and others. Practice shows that this improvement of environmental factors is not always associated with protecting the health and safety of workers practicing "green" professions, so it is necessary to focus efforts in this direction in order to ensure occupational safety and health (OSH). In this regard, an overview of the production line for high purity polyethylene terephthalate (PET) flake is presented in [III.11]. The stages of processing, the dangers for the workers, the preconditions for ensuring OSH, and the ecological and economic efficiency of the production line are considered.

Tourism, as one of the priority industries, is becoming increasingly important for the successful economic development of the country and in particular in the specific settlements. The existing natural resources for the development of tourism in accordance with the ecological and natural resources of the country were analyzed and the results of the research and analysis of the existing natural, cultural-historical, climatic-geographical, infrastructural and other resources for the region of Bov were presented [II.3]. In 2018, the route of the tourist trail "Pod kamiko" in the same settlement was considered. An assessment of the opportunities for sustainable development of eco-tourism is made, reflecting the changes that have occurred since the construction of the tourist trail in 2012. The result of the situational analyzes of the strengths and weaknesses of the site and opportunities and threats caused by external factors (SWOT analyzes), before and after the construction of the path were presented. The results of conducted surveys on the impact of the route on tourism and the development of the settlement and the changes in the profile of the tourist flow were also presented [III.7].

Based on the conducted research, the achieved contributions can be summarized in two directions:

Scientific-applied achievements (contributions):

1.   A matrix for forming glassy samples for wave-dispersive X-ray fluorescence analysis has been designed and fabricated, and compositions for secondary standard samples for characterization of molybdenum concentrate have been modeled. The obtained samples were implemented in the production process.

2.   A compositions for multicomponent mixtures with possibility of application in soil-chemical practice are modeled in order to improve composition and properties of real soils. Data have been obtained proving the possibility for their practical applicability, incl. for increase the nutrient and carbon content in tests in green peas (*Pisum sativum*) and sweet pepper (*Sweet pepper*).

3.   It was cultivated fungus (Pleurotus ostreatus) on substrates of various organic wastes and composts. A fungus (Pleurotus ostreatus) was cultivated on substrates of various organic wastes and composts. It has been found that the dense substrate-mycelial blocks can be applied in the environment of solid waste products, as well as directly in the environment of contaminated soils, which is a perspective method for bioremediation.

Scientific achievements (contributions):

1.   For the first time in the country, for conducting of wave-dispersive X-ray fluorescence analysis, modeling of the composition of secondary standard samples, resembling the matrix composition of real soil was performed. For the purposes of quantitative determination of the heavy metals present in the analyzed contaminated soils, the method of the standard curve, prepared on the basis of the developed secondary standard samples, has been applied.

2.   For the first time a simulation of the process of fluid flow through a porous medium, the boundary conditions of which correspond to the parameters of a natural soil system, has been performed. The ANSYS Workbench CFX modeling and simulation program was used for this purpose. The data from the initially established model are applicable as a basis for further refining and establishing the specific parameters of the porous body, which fully correspond to the parameters characteristic of a real soil system.

3.   Based on the conducted researches for characterization of various materials, wastes and soils, it was obtained new data on the composition and properties of:

- *composts obtained on the basis of various raw materials and production processes;*
- *contaminated soils from the area of the metallurgical plant "Eliseina";*
- *soils form the "Srebarna" National Natural Reserve;*
- *soils and food samples (meats) from different areas of the country;*
- *waste olive meals;*
- *building mixtures;*
- *surface and drinking waters from the area of the village of Bov.*

4.   The parameters of the combustion process and the energy value of olive meal at different initial moisture content have been calculated. Recommendations have been made for utilization of the energy potential of the generated olive meal.