MINISTRY OF EDUCATION AND RESEARCH

INSTITUTE OF CHEMISTRY

The title of manuscript:
U.D.S. 504.45.06(043.2) +579.22:546.3(043.2)

ZINICOVSCAIA INGA

IMPACT OF SOME METALS DETERMINED BY NEUTRON ACTIVATION ANALYSIS ON THE QUALITY OF THE ENVIRONMENT

145.01. ECOLOGICAL CHEMISTRY

Doctoral thesis in chemistry

CHISINAU, 2022

The thesis was performed in the Institute of Chemistry

Scientific adviser:

DUCA Gheorghe, dr. hab. in chem., univ. prof., acad., Institute of Chemistry

Official opponents:

CIOBANU Mihail, dr. hab. in chem., assoc. prof., Institute of Chemistry

COVALIOVA Olga, dr. hab. in chem., assoc. prof., Institute of Chemistry

GONTA Maria, dr. hab. in chem., univ. prof., Moldova State University

Composition of the Specialized Scientific Council:

President

LUPAȘCU Tudor, dr. hab. in chem., univ. prof., acad., Institute of Chemistry

Scientific secretary

BUNDUCHI Elena, dr. in chem., assoc. prof., Moldova State University

Members

STURZA Rodica, dr. hab. în șt. chim., univ. prof., Technical University of Moldova

BULIMAGA Constantin, dr. hab. in biol., assoc. prof., Institute of Ecology and Geography

POVAR Igor, dr. hab. in chem., assoc. prof., Institute of Chemistry

DULIU Octavian-Gheorghe, dr. in phys., dr in geol., univ. prof., University of Bucharest, Romania

The defense will take place at **November 28, 14.00** at the meeting of the Specialized Scientific Council **DH 145.01-22-4** of the Moldova State University, A. Mateevici 60 Str., block 4, room 222, Chisinau, MD-2009.

Thesis and abstract are available in the library of the Andrei Lupan Central Scientific Library (MD 2028, Chișinău, Academiei str. 5A), Central Library of the Moldova State University (MD 2009, Chișinau, Alexei Mateevici str. 60) and on the web page of ANACEC. (www.cnaa.md).

Abstract was sent on **October 25, 2022**

Scientific secretary
Specialized Scientific Council
dr. in chem., **BUNDUCHI Elena**

Scientific adviser:
dr. hab. in chem., prof. univ., acad. **DUCA Gheorghe**

Author: **ZINICOVSCAIA Inga**

CONTENT

CONCEPTUAL MILESTONES OF THE RESEARCH

Background and importance of the topic discussed

Today, environmental pollution has become increasingly prominent in many countries of the world. Traditionally, pollutants such as sulfur dioxide and carbon dioxide, have been put under control, however, pollution of different environmental compartments (air, soil, and water) with heavy metals, which leads to ecosystems deterioration and possess a serious threat to food security and human health, have yet to gain policymakers' attention [1]. Since the environment is the habitat of humans, plants, animals and microorganisms it is very important to maintain its chemical composition to be adequate to the biologic value of habitation. This is possible by the monitoring of the state of the environment and suggestion of the way of reduction of contaminants level in order to prevent environmental pollution and to ensure sustainable development. The solution to this problem is the exceptional prerogative of ecological chemistry, which is focused on the urgent need for economical development and appropriate environmental impacts, which need to be addressed [2].

Environmental pollution with heavy metals is associated with rapid development in industry and agriculture, as well as disturbance of the natural ecosystem due to the enormous growth in the world population [3]. At the same time, the knowledge on emissions and emissions sources of heavy metals is still limited and incomplete concerning the information on emissions source categories and emission generating processes [4]. Every year, air pollution causes nearly 500 000 premature deaths and annual urban levels of PM_{10} monitored in over 1790 cities in 42 countries generally exceed the World Health Organization (WHO) guidelines value [5]. Nowadays, there are around 5 million sites of soil pollution covering 500 million ha of land, in which the soils are contaminated by different heavy metals or metalloids in concentrations significantly overpassing the geo-baseline or regulatory levels. Heavy metal pollution in soil has a combined worldwide economic impact estimated to be over US$10 billion per year [6]. In high-income and upper-middle-income countries of the WHO European Region, about 30% and 60% of urban wastewater, respectively, is released to the environment without preliminary treatment, leading to contamination of natural water bodies and soil with harmful compounds, especially heavy metals and creation of unbalanced ecosystems.

Nowadays, in many countries, norms and regulations attempt to ensure that adverse impacts of environmental pollution are minimized, starting with the planning stage, choice of location, and adoption of the best available technologies. This, however, is not always the case, especially when old technologies continue to operate in populated areas or when norms and standards are weak or not complied with and significant emissions occur [7].

Currently, air pollution is one of the most serious problems in the Republic of Moldova and particularly in Chisinau. According to the national reports, in air samples mainly the concentrations of particulates, sulfur dioxide, carbon monoxide, nitrogen dioxide, phenols, and formaldehyde are determined [8,9]. At the same time, information concerning the determination of heavy metals is very limited.

Along with air, the soil is another media, rigorously investigeted using approaches of ecological chemistry, significantly affected by anthropogenic activities [10]. Soil acts as a sink and also as a source of pollution with the capacity to transfer pollutants to groundwater and the food chain, and then to humans and/or animals. Anthropogenically derived heavy metals into the soil and could be easily transported via the root system into the plants where they accumulate into their different parts including fruits. Contaminated vegetables, fruits, medicinal plants can cause serious clinical and physiological problems for humans, especially when consumed in large quantities. Environmental and food safety are increasingly attracting the attention of the public, and there is greater interest in the analysis of the elemental content of soil and agricultural products and to assess elements transfer from soil to crops [11].

The applications of metals in different industrial processes and inappropriate wastewater treatment resulted in a significant increase in their environmental levels relative to the normal background. The presence of heavy metal ions in wastewaters represents a hazard to the aquatic ecosystem and raises many risks for human beings. Since wastewater often are used for irrigation, they have a negative impact on the soil and agricultural products as well. Thus, it is important to reduce the level of heavy metals to maximum admissible levels before their discharge.

It is evident that the pollution of one of the environments' compartments with heavy metals in a consequence will result in metal migration into the other media and would significantly increase the burden on the environment and society. Thus, it is important to monitor the level of air, soil, and water pollution with heavy metals, to identify sources of pollution, and develop the approaches of metal concentration reduction to admissible levels.

The aim of the present thesis was to determine the content of some chemical elements using neutron activation analysis in different environment' compartments in the Republic of Moldova in order to define the biological value of the environment, to assess the risk on human health as well as to develop the technology of metal removal from industrial effluents using different types of biological sorbents.

To achieve this purpose, it was necessary to solve the following **objectives**:

- to perform passive and active biomonitoring studies in the Republic of Moldova and to determine the elemental composition of moss samples;
- to apply statistical tools and GIS technologies to pinpoint possible air pollution sources;
- to calculate the relative accumulation factor and non-cancer health risk of air pollution with elements, considered as environmental pollutants on human health;
- to determine the content of elements in soil, fruits, leaves, juice, wine, and medicinal plants samples collected in the Republic of Moldova
- to establish the relation between metal concentrations in soil, fruits, juice, and wine samples;
- to calculate the hazard index values for elements in fruits and medicinal plant in order to establish their impact on consumers' health;
- to determine the metal sorption capacity of different type of biosorbents as a function of different physico-chemical parameters and to evaluate adsorption character using different kinetics models, models of adsorption isotherms as well as to calculate the thermodynamic of the process.
- to determine optimal conditions for effective metal ions removal from industrial effluents.

The hypothesis of the research

Since the anthropogenic pressure on the environment has increased in the recent decades, environmental protection become a priority task for many countries around the world. It is supposed that the current level of heavy metals emission by vehicles, industrial and agricultural sector in the Republic of Moldova has a negative effect on the quality of the environment and human health.

The obtained result, which contributes to the creation of the new scientific direction: application of neutron activation analysis in estimation of the biological value of the habitate for life based on the determination of the elemental composition of the different environmental samples.

The synthesis of the research methodology and justification of the research methods

The concept of the research was developed following the ideas presented by acad., prof. Gheorghe Duca in "Ecological Chemistry" (DUCA Gh. Ecological Chemistry. Chişinău: CE USM, 2002, 289 p.). Air quality in the Republic of Moldova was monitored by two techniques passive and active moss biomonitoring. The idea of using mosses to estimate atmospheric heavy metal deposition was developed in the late 1960s by Rühling and Tyler (RÜHLING, Å., TYLER, G. An ecological approach to the lead problem. In: *Botaniska Notiser*. 1968, nr. 122, pp. 248-342). To assess air quality in urban areas active biomonitoring using the ‘‘bags technique’’ developed by (GOODMAN G.T., ROBERTS T.M. Plants and soils as indicators of metals in the air. In: *Nature* 1971, nr. 231, pp.287–292) was applied. This technique has several advantages: well-defined exposure time, known background concentrations of elements in the moss, flexibility in site selection and number of sampling sites to be chosen, uniformity of entrapment surface, etc

To determine the elemental content of moss samples, soil, agricultural crops, wine neutron activation analysis at the IBR-2 reactor was used. It is a high-sensitive, non-destructive technique, which allows simultaneous determination of more than 40 elements in samples, without their preliminary chemical pretreatment. The main features of the method as well as technical parameters of the used technique are presented in (FRONTASYEVA M. V. Neutron Activation Analysis in the Life Sciences. A review. In: *Physics of Particles and Nuclei,* 2011, Vol. 42, No. 2, pp. 332-378).

To assess the quality of the air and soil several pollution indices (Geo-accumulation index; Enrichment factor, Contamination factor, Pollution load Index) were calculated. To characterize the relationship between the elements in soil, leaves, fruits, wine the transfer factor introduced by Kiekens and Camerlynck (KIEKENS L., CAMERLYNCK R. Transfer characteristics for uptake of heavy metals by plants. In*: Landwirtschaftliche Forschung*, 1989. nr. 39, pp. 255–261) was used. For fruits, the daily intake of metals and the hazard quotient indices were calculated.

Metal removal from wastewater was performed through biosorption and bioaccumulation processes. The application of biological objects for metal removal can be explained by their abundance, simplicity of the experiments, high removal efficiency, and environmental safety. Atomic absorption spectrometry was used complementary to neutron activation analysis to assess the efficiency of metal removal from single-component solutions.

The present thesis was performed under an agreement between the Institute of Chemistry and the Joint Institute for Nuclear Research, Dubna, Russia. The irradiations of the samples for the thesis were carried out at the reactor IBR-2 of the Frank Laboratory for Neutron Physics and 3 MV Tandetron accelerator of Horia Hulubei National Institute of Physics and Nuclear Engineering, Magurele Romania.

THESIS CONTENT

1. METALS IMPACT ON THE ECOLOGICAL SYSTEMS

The chapter comprises the state-of-the-art on the issues discussed in the thesis. The most important metal emission sources are highlighted and the effect of the metal ions on human health is described. The analytical techniques widely applied for the determination of the elemental content of environmental samples, their advantages and limitations are given. Monitoring of the air quality is a complex technical task, cheap and efficient techniques for tracing atmospheric contamination, namely active and passive biomonitoring, are described in detail, and examples of their application in different countries are provided. The approach of calculation of non-cancer toxic risk on human health associated with metal ions inhalation, ingestion, and dermal contact are presented. The sources of soil and agricultural crops pollution with heavy metals are emphasized. The most widely applied indexes for the assessment of the level of soil pollution and calculate the non-carcinogenic risk of toxic elements are presented. Examples of studies dealing with the determination of elements content in soils and agricultural crops as well as metal bioaccumulation in soil-agricultural crops systems are presented. The principal sources of metal ions in water are highlighted. The parameters which affect metals biosorption, pH, metal concentration, time of contact, and temperature, are described in detail. The models used to describe equilibrium, kinetics, and thermodynamics of the sorption process are presented. The literature review presented in this chapter provides important theoretical support for the research reflected in the further chapters.

2. MATERIALS AND METHODS

In this Chapter description of the main chemical and standard reference materials used in the study is given. The chemical composition of wastewater obtained from several industrial companies is presented. The principle of neutron activation analysis, its advantages and limitations, and the procedure of method implementation on the installation REGATA of the IBR-2 reactor are described in detail. The procedure of samples collection and preparation for neutron activation analysis is given. The details of samples preparation and measurement using atomic absorption spectrometry are highlighted.

3 ASSESSMENT OF AIR POLLUTION IN THE REPUBLIC OF MOLDOVA

3.1. Assessment of heavy metal pollution in Moldova using passive biomonitoring

Chapter presents the results of passive and active biomonitoring studies performed in the Republic of Moldova. In 2015, the RM for the first time joined the moss survey in the framework of the International Cooperative Programme on the effects of air pollution on natural vegetation and crops with heavy metals in Europe (UNECE ICP Vegetation). Thirty three samples of moss *Hypnum cupressiforme* were collected in May 2015 throughout the territory of the country (Fig.3.1). The moss sampling and further preparation for elemental analysis were done following the CLRTAP [12] manual for moss sampling. Elemental composition of mosses was determined by neutron activation analysis.

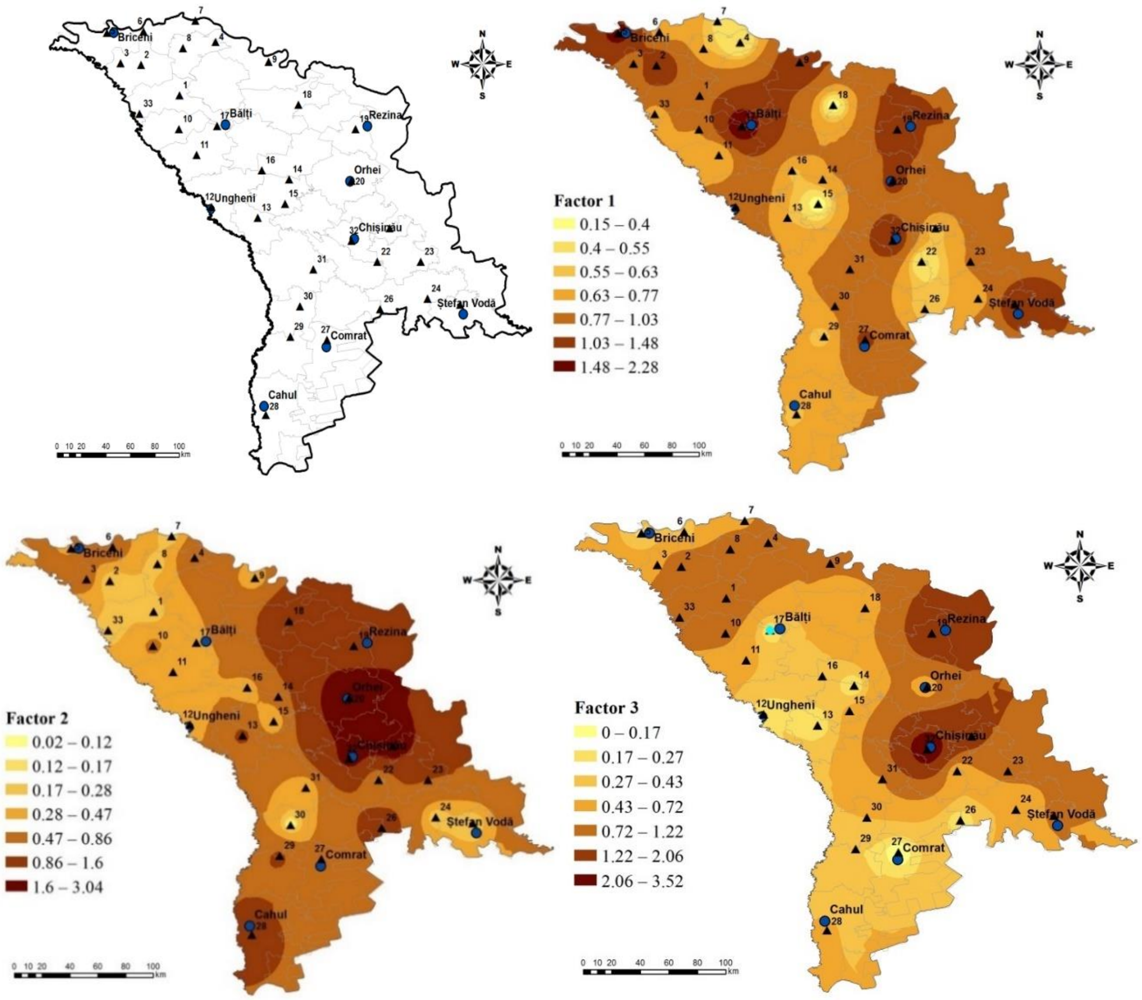

Fig. 3.1 Location of sampling points in Moldova during the moss survey 2015/2016 and spatial distribution of Factor 1-3 scores.

A total of 37 elements were determined in the collected moss samples by NAA and 3 elements by AAS. Table 3.1 summarizes the results regarding the content of 41 elements, mean, minimum, maximum and coefficient of variation.

Table 3.1 Descriptive statistics of measurements for moss samples (mg/kg)

Element	Max	Min	Md	CV	Element	Max	Min	Md	CV, %
Na	2110	151	308	81	**Sr**	125	21	41	48
Mg	905	182	328	49	**Zr**	126	5.0	14	102
Al	17200	1560	3120	79	**Cd***	0.95	0.2	0.39	40
K	9670	2610	7110	29	**Sb**	1.1	0.1	0.2	69
Cl	373	46	104	67	**Ba**	137	25	61	45
Ca	17200	5320	9880	26	**Cs**	1.4	0.15	0.3	73
Sc	3.3	0.3	0.6	75	**La**	11.7	0.9	2.1	79
Ti	1300	103	232	81	**Ce**	27	1.9	4.4	82
V	29	2.9	5.5	80	**Nd**	10.7	0.5	1.9	88
Cr	33	2	7.2	72	**Sm**	1.6	0.1	0.3	80
Mn	401	42	120	56	**Eu**	0.4	0.02	0.07	84
Fe	9200	1010	2130	72	**Gd**	1.5	0.04	0.2	92
Ni	17	2.3	4.7	62	**Tb**	0.3	0.02	0.05	82
Co	4.7	0.4	0.8	74	**Tm**	0.1	0.01	0.03	85
Zn	79	20	37	33	**Yb**	0.9	0.06	0.2	81
Cu*	28	5.9	14.7	33	**Hf**	3.3	0.17	0.47	92
As	4.06	0.4	0.8	66	**Ta**	0.3	0.03	0.06	80
Se	0.4	0.2	0.3	21	**W**	1.1	0.1	0.2	70
Br	9	1.6	4.7	35	**Pb***	27	5.4	12	37
Rb	31	4.3	9.8	61	**Th**	3.8	0.27	0.65	81
					U	1.25	0.1	0.23	75

*- determined by AAS; min - minimum; max - maximum; Md - median; CV - coefficient of variance.

Data analysis was performed using the Factor analysis, which results are given in Table 3.2.

Factor 1 (Fig. 3.1), representing 53% of total variability, includes elements such as Al, As, Fe, Ti, V, Cr, Co, Ni, Cs, La, Th, and U, and can be considered as a combined geogenic/anthropogenic association of elements. The elements (Al, Fe, Ti, Cs, La, Th, U) are typical crustal elements and their content in the mosses can be associated with soil particles release into the atmosphere by wind, mainly in the area with dry climate and low rainfall. The high concentrations of some elements (Fe, Cr, As, V, and U) near Chisinau and Balti also indicate the possible influence from anthropogenic sources. Chisinau and Balti are characterized by high traffic density and high emissions of industrial pollutants. High content of As and U were determined near Chisinau where the Combined Heat Power Plants No.1 and No. 2 are operated. High levels of V and Ni, near Balti, can be associated with the burning of heavy fuel oil for heating and electricity production at the North Combined Heat Power Plant. Iron and Cr emissions near

Chisinau and Balti may be associated with the of SA “Moldagrotechnica” in Balti, SA “Moldovahidromas” in Chisinau and other small industrial enterprises. Relatively high content of V, As and U almost on the whole territory of the country can be explained by use of coal and wood for heating in rural area.

The second factor F2 (Fig.3.1) represent 10% of variability and includes elements Cl, Se, and Sr. The high content of the above-mentioned elements is explained by their leaching from higher plants or penetration from the soil. At the same time, it should be mentioned that the important source of Se can be coal burning. Again, the Chisinau area is the most polluted as here the human influence on the environment is significant.

Factor 3 is an anthropogenic component with high values for Pb, Sb, and Zn with 16% of the total variance. Higher Pb content have been found in the densely populated and industrialized parts of the Moldova (Chisinau, Rezina, Ungheni, Stefan Voda). The highest Pb values were registered in the zone Causani-Stefan-Voda. Antimony is a toxic trace element, commonly enriched in coals, and fossil fuel. Sb is also used in alloys, ceramics, glasses, plastics, and synthetic fabrics production. The highest Sb values were determined in Chisinau and Balti. The highest levels of Zn found in Rezina town can be explained by the influence of the metallurgical industry located in Ribnita.

To quantify the anthropogenic influence on the environment, Contamination Factor (CF), Geochemical index (I_{geo}), and Pollution load index (PLI) values were calculated for the entire country as well as for Chisinau and Balti separately (Table 3.2). Ten elements were taken into account, which can be emitted by the industrial activity and are considered the environmental pollutants. The C_F values obtained for all elements for the entire country lied between 1 and 2 indicating the moderate pollution of the territory. C_F values for Chisinau ranged from 0.52 for Cd to 9.1 for U, and for Balti from 0.33 for Cd to 8.6 for V. The increased content of U in the vicinity of Chisinau could be attributed not only to its release from the soil but also to power plants in the process of coal burning. The highest C_F value in Balti was obtained for V, the main source of which can be considered fuel combustion. I_{geo} values for the entire country were ≤ 1.0, except U, indicating that mosses were unpolluted to moderately polluted with analyzed metals. Uranium values of (1.5) indicated the moderate country pollution and the strong environment pollution around Chisinau with I_{geo} value 3.6 According to I_{geo} values for Pb, Cd, U, Zn and Cu in Balti there is no significant contamination with these elements. For other elements, pollution can be classified as moderate. The PLI values similarly indicated moderate to severe pollution, especially in Chisinau where the main contribution comes from U.

Table 3.2 Average values of the C_F, I_{geo} and PLI for entire Republic of Moldova, Chisinau and Balti municipalities

Element	Moldova		Chisinau		Balti		Element	Moldova		Chisinau		Balti	
	C_F	I_{go}	C_F	I_{go}	C_F	I_{go}		C_F	I_{go}	C_F	I_{go}	C_F	I_{go}
Al	1.5	0.58	5.1	Zn	7.2	2.85	Zn	1.2	0.26	2	1.00	1.6	0.68
V	1.2	0.26	4.1	Sb	8.6	3.1	Sb	1	0.00	4.7	2.23	3.5	1.81
Cr	1.7	0.77	7.6	Pb	5.8	2.54	Pb	2	1.00	1.9	0.93	1.1	0.14
Fe	1.6	0.68	6.7	U	6.5	2.70	U	1.7	0.77	12.5	3.64	1.5	0.58
As	1.3	0.34	6.7				*PLI*	1.44		4.89		3.38	

Important task of ecological chemistry is not only determination of the chemical composition of the environment, but also estimation of the risk of pollution and its impact on human health. To assess the negative effect of elements considered as environmental pollutants, which can find their way in the human body *via* ingestion, dermal contact and inhalation the average daily dose (ADD) values were calculated which showed that the ADD of ingestion for all metals was significantly higher than those of inhalation and dermal absorption. According to calculated data for all elements, except V for children, Hazard Quotient (HQ) and Hazard Index (HI) values were lower than 1.0, indicating that there is no significant health risk associated with these elements. The orders of HI of metals decreased in the order: V>As>Fe>Cr>Sb>Pb>Cd>Cu>U>Zn for children and V>Cr>Pb>Zn>U>Fe>As>Cd>Cu>Sb for adults. For children, HI values of V were higher than 1.0, indicating its potential danger for children's health.

3.2. Active biomonitoring in an urban area: Chisinau case study

To examine the ecological situation in Chisinau, the active biomonitoring using the “moss bag technique” was applied. Moss *Sphagnum girgensohnii* (Russow) collected in a pristine wetland located in the Tver region, Russian Federation and packed in nylon net bags was exposed at three site: the thermal power plant (TPP), and the Academy of Sciences main building (AS) as potentially polluted places, and in the Botanical Garden (BG) considered as an unpolluted site (Fig. 3.2) from October 2016 to March, 2017. A part of the unexposed moss material was kept in the laboratory and further used as a reference sample. Elemental composition of exposed and unexposed mosses was determined by NAA.

Fig. 3.2 Exposure sites of the *S. girgensohnii* moss bags: I (TPP), II (BG) and III (AS).

The concentrations of the main part of elements in the exposed moss samples were higher than in the control sample indicating that the sites, where the moss bags were exposed, can be contaminated by the elements in question. The change of the content of elements V, Ni, As, Sb, Pb, Fe, Cu, and Cr is presented in Fig. 3.3. The most pronounced increase of V content was observed at the TPP place, confirming that the combustion of fossil fuels is one of the main air pollution sources in Chisinau. The content of V in moss increased by 3.7-20 times. A maximum amount of V was accumulated in moss after 4 months of exposure. The high content of V in January and February can be explained by the low outside temperatures and consequently, more intense heating. Vanadium content almost did not change at the BG site, its content in moss increased by 1.4-1.7 times. The increase of V content at AS site by 1.5-4.1 times can be explained by windblown dust and proximity to the TPP site.

Content of Ni increased at all exposure sites: by 2-5.9 times at TPP, 1.5-4.5 times at BG, and 2-4 times at AS. Its highest level was observed at the TPP site, with the maximum amount accumulated in November (4.7 mg/kg). The continuous increase of As content at the TPP site by 1.1-1.4 times in comparison with control was detected. At the BG site (except the first month) and at the AS site the As content was lower than in the control sample. A significant increase of As in the first month at the BG site (1.7 times) can be connected with its accumulation from soil particles. It should be mentioned that the trend of As and Ni accumulation in moss samples was approximately the same indicating a common source of pollution. The significant increase of Sb at TPP site (8.3-33 times) can be explained by coal burning and traffic emissions. High accumulation of Sb at the BG (3-10 times) and AS (15-43 times) sites could be associated with transport and vehicle components as well as its natural release from the earth's crust.

Continuous accumulation of Pb moss at all three sites indicates use of lead-loaded gasoline in Moldova. The emissions from traffic, besides Pb, contain many toxic heavy metals such as Cd, Sb, Ba, and Zn. Lead content in moss exposed at TPP increased 9.8-15 times, at BG site 5-14 times, and at AS site 6-17 times. The highest accumulation of Fe was noticed at AS site, 7 times higher in comparison with control, at TPP the increase was 2-5 times higher and 2-3 times higher at the BG site. Continuous increase of Cu and Cr content at the TPP site was observed: 4-14 times and 2-3 times in comparison with control, respectively. At AS site the maximum amount of both elements was accumulated in January (4 mg/kg of Cr and 8.6 mg/kg of Cu), then their content was decreased. At BG site Cr content increased by 1.5-3 times, while Cu by 6-9 times.

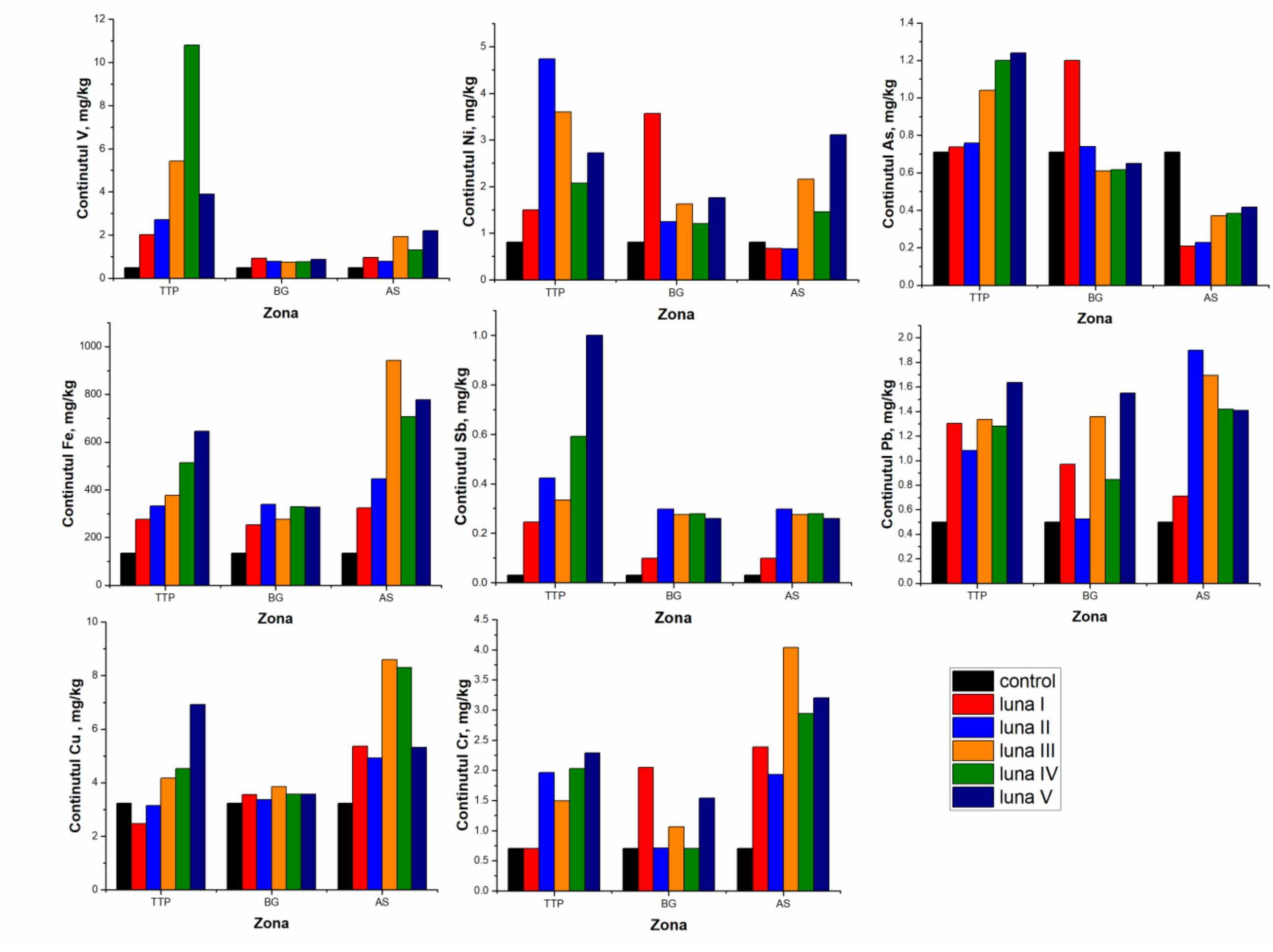

Fig. 3.3 Content of the elements in moss bags exposed for 5 months at three sites: TPP, BG, and AS.

The risk of human exposure to the determined levels of elements content was assessed. The values for ADD of ingestion for all metals were higher than those of inhalation and dermal absorption. The highest average values of HQ were found to be through the ingestion pathway followed by the dermal contact and inhalation. For all elements, except of V, HQ and HI values were lower than 1.0, indicating that there are no significant health risks from these metals. At the same time, it should be mentioned that HI and HQ values higher than 1.0 for V were only at the TPP site, confirming that the combustion of fuel (coal, oil) is the main source of air pollution with V in Chisinau. The orders of hazard indexes of metals were V>Sb>As>Cr>Fe>Pb>Ni>Cu at TPP site, V>Sb>As>Cr>Fe>Pb>Cu>Ni at BG site and V>Sb>As>Cr>Fe>Pb>Cu>Ni at AS site. Thus, it can be seen that V, Sb, and As are the main air pollutants in Chisinau.

4. ECOLOGICAL CHEMISTRY OF SOIL AND FOODSTUFF PRODUCTS

4.1 Analysis of the elemental composition of soil and wine from Cricova and Romanesti and their classification according to provenance

The chapter is devoted to the assessment of the quality of soil and agricultural crops collected in the Republic of Moldova (RM). Twenty-four samples of red and white wine and 18 samples of soils obtained directly from two major wine-producers: S.A. Romanesti and S.A. Cricova were analyzed to determine their elemental composition as well as to use these data in an attempt to differentiate them by region and by types. From the Romanesti company 13 samples were analyzed: Cabarnet, Regent, Pinot Noir, Nero, Syzar, Merlot, Malbec, Sauvignon, Riesling, Sauvignon, Pinot Gris, Muscat, UniBlanc and from Cricova company - 11 samples: Pinot, Chardonnay, Cabernet, Chardonnay, Pinot Frank.

Applying NAA it was possible to determine 35 elements in analyzed soil: seven major, rock-forming elements: Na, Mg, Al, Ca, K, Mn and Fe and 28 trace elements: Sc, Ti, V, Cr, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Tm, Yb, Hf, Ta, Th and U. The similarity in the elemental composition of soils (Fig.4.1) obtained from two companies can be explained by the vicinity of two vineyards, which are located at a distance of about 15 km from each other.

To evaluate the pollution of soil collected in vineyard area the data obtained for elements considered as possible environmental pollutants, Cr, Mn, Co, Ni, Zn, Sb, and As, were compared with the maximum admissible concentrations established by the National Authorities of Moldova [13] and neighboring counties: Romania [14] and Russian Federation [15] (Table 4.1).

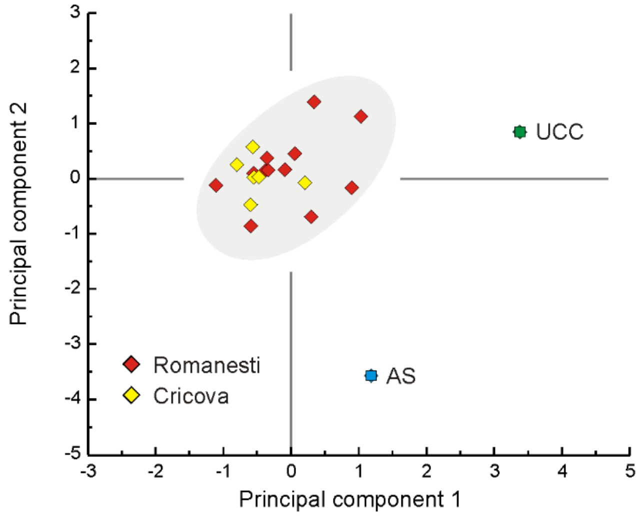

Fig. 4.1 The bi-plot illustrating the homogeneity of the soil samples

Except for As, whose content in the soil of all the vineyards was about 8 mg/kg, the content of all possible industrial pollutants felt in the limits established for the RM and other countries.

Table 4.1 The average values (± SD) of the content of possible pollutants in the analyzed samples well as the corresponding maximum admissible limits

Element	Analyzed soil	Moldova	Russian Federation	Romania
	Concentration, mg/kg			
Cr	91 ± 9	90	6*	30 - 100
Mn	678 ± 56	1500	1500	900 - 1500
Co	13 ± 1	--	5	15 - 30
Ni	35 ± 7	45	20 - 80	20 - 75
Zn	72 ± 10	68	55 - 220	100 - 300
Sb	0.9 ± 0.1	-	4.5	5-12.5
As	8.7 ± 1.1	5.6	2 - 10	7

A common approach to estimate the anthropogenic impact on soil is to calculate Enrichment Factor (EF) values for metal concentrations above uncontaminated background levels. Iron has been used for the calculation of the EF. Calculated EF values indicate the minor soil contamination. The I_{geo} values for all elements, except As, were less than 1.0, pointing at an uncontaminated environment. The value obtained for As (1.85 ± 0.16) is characterized as a moderately contaminated medium. PLI value (1.15 ± 0.11) suggests weak soil pollution.

Table 4.2 Average values (±SD) of the EF, I_{geo}, and PLI of the investigated vineyards soils

Element	EF ± SD	I_{geo} ± SD	PLI ± SD
Cr	1.29 ± 0.12	-0.62 ± 0.15	
Mn	1.18 ± 0.13	-0.75 ± 0.12	
Co	1.01 ± 0.06	-0.97 ± 0.13	
Ni	0.84 ± 0.10	-1.24 ± 0.24	
Zn	1.33 ± 0.14	-0.58 ± 0.22	
As	7.14 ± 0.47	1.85 ± 0.16	
			1.15 ± 0.11

From the data presented in Table 4.3, it can be seen that from 18 elements determined in wine samples the highest values were obtained for K, its values in wines varied from 253 to 843 mg/L. The highest K content was determined in Syzar and Malbec wine samples (Romanesti company).

Table 4.3 The mean experimental values (± σ) of the concentrations of 18 elements in investigated wines as determined by the NAA as well as values established by OIV [16].

Element	Romanesti red	Romanesti white	Cricova red	Cricova white	OIV
Concentration, mg/L					
Na	19±9	16±1	11±2	11±3	80
Mg	104±12	87±12	77±5	92±21	
Al	1.4±1	1.9±0.5	1.4±1	1.5±0.7	
K	690±80	380±230	460±80	550±100	
Ca	54±14	75±24	66±13	68±21	
Cl	14±5.9	4.5±3.7	2.3±1.15	6.3±3.2	
Mn	1.35±0.1	1.22±0.25	0.93±0.1	1±0.2	
Fe	3.5±3.3	2±1.9	1.1±0.7	0.7±0.4	
Zn	0.44±0.2	0.55±0.04	0.92±0.4	0.49±0.08	5
Rb	1.7±0.2	1.1±0.4	1.6±0.3	1.6±10.3	
Sr	1.01±0.2	0.64±0.2	0.84±0.3	0.75±0.15	
Concentration, µg/L					
Co	6.3±3.6	9.8±1.4	4.2±1.6	3.2±0.7	
Ni	39±10	32±11	18±9	20±5	
As	-	-	0.29±0.2	0.3±0.1	200
Br	280±90	92±92	69±25	104±44	1000
Sb	0.48±0.2	0.41±0.13	0.59±0.4	0.53±0.26	
Cs	3.3±0.6	3.1±2.5	7.5±2.8	6.1±1.1	
Ba	276±270	110±30	70±41	87±27	
U	0.12±0.06	0.20±0.06	0.13±0.04	0.13±0.01	

Sodium content in analyzed wine samples varied from 8 to 32 mg/L with the highest concentrations coming from Cabarnet, Regent, and Uniblanc wines. Magnesium, which content in wine is affected by the grape variety, the winemaking process, wine storage, and the use of ion-exchange resins in the studied wines varied between 65 and 132 mg/L. Calcium concentration in studied wines lies within the range of 29-121 mg/L. Iron content in wines varied from 0.15 to 8.8 mg/L, with the maximum values in Cabernet, Pinot Noir, and Malbec wines (in these wines the concentration of iron was higher than 5 mg/L). In analyzed wines, Mg concentration varied from 0.7 to 1.6 mg/L with the highest value for Pinot Noir (Romanesti). The data obtained for Zn does not exceed values recommended by International Organization of Vine and Wine (OIV) and are in the range 0.2-1.3 mg/L.

Among the microelements, the most abundant were Ba and Al. Arsenic, a toxic element, was present in an insignificant concentration only in the wines from the Cricova company (0.16-0.63 µg/L).

The Discriminant Analysis (DA) was used to differentiate the investigated wines by sort and by location. The results obtained are illustrated by the discriminating Root 2 x Root 1 bi-plot reproduced in Fig. 4.2.

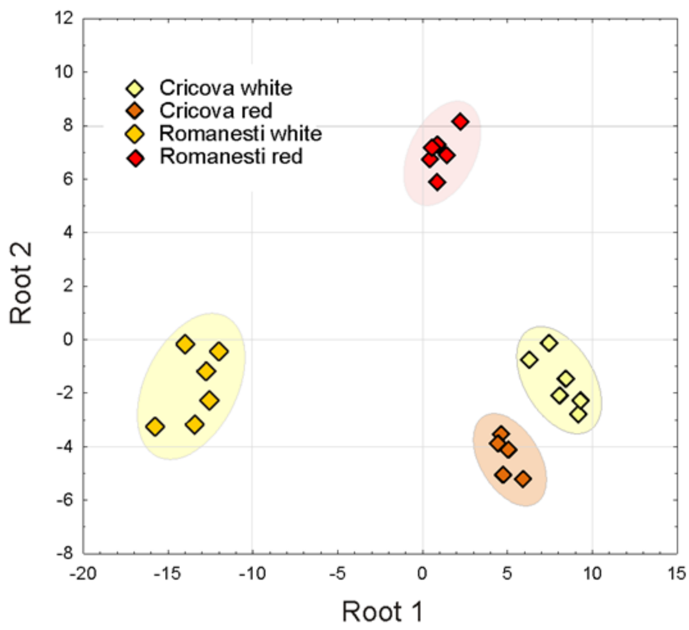

Fig. 4.2 The discriminating Root2 vs. Root 1 bi-plot illustrating the result of Discriminate Analysis of the 24 sets of wines.

The Root 1 allowed the complete discrimination between the Romanesti white wine and all other ones while Root 2 better evidenced the Romanesti red wines. At the same time, from this point of view, the Romanesti wines seem to be more different between them with respect to the type while Cricova ones form a most compact group. Regardless of these considerations, the DA allowed the simultaneous discrimination of all types of wine on varieties: red and white as well as on vineyards: Romanesti and Cricova.

To characterize the relationship between the soil and the wine as the final product of the grape-wine, the Transfer Factor (TF) values were calculated. The values of TF for Na, Mg, K, Ca, Mn, Zn, Rb, Sr, and Br were higher than 1.0. The highest TF values belonging to K were found in all wines: 36 ± 5 for Romanesti red wine and 32 ± 6 for Cricova white wine. High TF was also obtained for Br (35 ± 12 mg/kg Romanesti red wine) and Rb: (17 ± 3 Cricova red and white wines). Arsenic, which was found only in the Cricova wine samples has a very low TF of 0.03 ±0.01 mg/L.

4.2. Assessment of metals accumulation in soil-leaves-grapes-must system

Since wine is a final product of grapes processing in the further study to trace the links of metal bioaccumulation in the system soil-leaves-grapes-must the grapes type – Ialovenschii Ustoicivii was selected. Soil, fruits and leaves of grape sampling was carried out in the Danceni village, Ialoveni district (the Central zone of the country). Elemental composition of collected samples was determined using NAA.

A total of 30 major and trace elements were determined in soils taken at the root of the vine. The content of microelements and trace elements (Mn, Ni, Cr, V, Ba, Zn, and La) in the soil corresponds to their content in common chernozems, characteristic for the RM. In grape samples using NAA it was possible to determine 25 elements and 26 elements in leaves samples. Among the determined major elements, K was the most abundant element in grapes, its content constituted 14500±725 mg/kg. The content of other major elements changed in the following order Ca>Cl>Ma>Na. Among the trace elements, the highest content in grapes was determined for Fe followed by Zn, Br, Mn, Cr, Mo, and Co. The content of almost all determined elements in leaves was significantly higher than in grapes. Calcium was the most abundant element in leaves with a concentration of 33400±1670 mg/kg, which can be linked to the rich limestone soil in Moldova. Relatively high Ca and Mg content in the leaves in comparison with fruits indicate their low mobility. Barium was determined only in the leaves samples.

Due to the fact, that the main part of grapes is industrially processed into beverages (wine, clarified, or combined juices) a particular interest represents the elemental content of juice as well as the transfer of elements from soil and fruits in juice. According to the data obtained the juice is characterized by high K content, followed by Ca, Cl, Na, and Mg. The content of microelements was changed in the following order: Fe>Br>Zn>Mn>Cr>Mo. The levels of rare earth elements and toxic metals (Sb) in all the samples were less than 0.01 mg/kg.

The values of TF were calculated to reveal the accumulation of elements in the following systems: $TF_{L/S}=C_{leaves}/C_{soil}$, $TF_{F/S}=C_{fruits}/C_{soil}$, $TF_{F/L}=C_{fruits}/C_{leaves.}$ The results obtained are shown in Figs. 4.3-4.4. According to the calculated values, leaves of the vines accumulate from soil predominantly Ca ($TF_{L/S}$ = 3.3), Sr ($TF_{L/S}$ = 2.8) and U ($TF_{L/S}$ = 1.0) (Fig. 4.3). The grapes accumulated K from soil with TF values 0.92 and for the other elements TF was less than 1.0, which indicates the lack of their accumulation in grapes. From leaves in grapes are accumulated Cl, K, Sc, V, Ta, and Th. The values for $TF_{juice/soil}$ and $TF_{juice/fruits}$ are presented in Fig. 4.4. As in the case of grapes, in juice is predominantly accumulated K from soil. For the main part of elements, $TF_{J/F}$ has values close to 1.0, indicating the lack of micro- and macro-elements losses in the technological process of industrial processing of grapes. The highest values were obtained for Na, Cs, Br and Co 4.2, 2.4, 2.1, and 1.8, respectively.

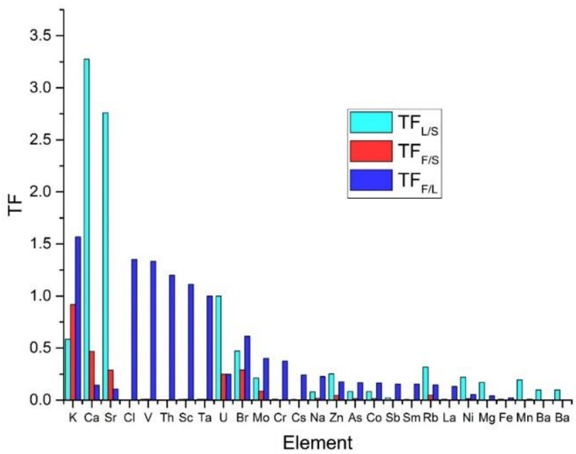

Fig. 4.3 Transfer factors values in system soil-leaves-grape

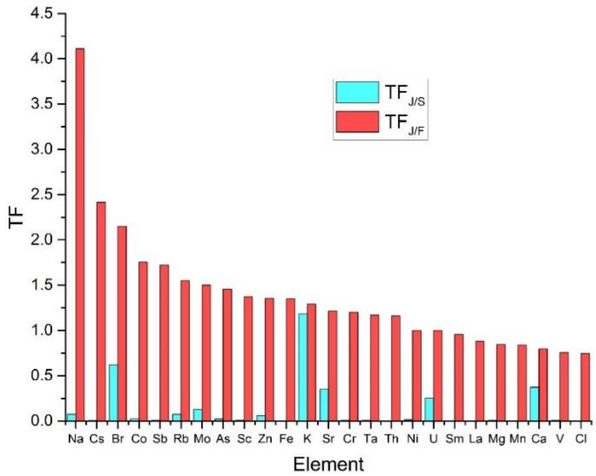

Fig. 4.4 Transfer factors in system soil-grape-juice

4.3 Determination of major and minor elements in fruits from different zones of Moldova by NAA and assessment of their provenance

To evidence any correlation between the different types of fruits and the place where were cultivated, fruits were collected in in four zones in the RM: South-East (Purcari), South (Cahul), Center (Ialoveni) and Codru (Criuleni). The following type and sorts of fruits were collected: in Purcari - the grapes Merlot (P_m), Feteasca Neagra (P_f) and Saperav (P_s); in Cahul – grapes ”Muscat de Hamburg” (C_{mh}), ”Moldova” (C_{md}), apples (C_a) and plums (C_p); in Ialoveni – grapes ”Alb de

Suruceni" (I_{as}), apples "Golden" (I_{ag}) and plums "Vengherca" (I_p); in Criuleni - grapes „Moldova" (C_{rmd}), apples (C_{ra}) and plums (C_{rp}).

The NAA allowed determining 22 elements (Na, Mg, Cl, K, Ca, Sc, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Sb, Cs, Ba, La, Th, and U) in the analyzed grape, apple, and plum samples. As in the case of fruits collected in Danceni district, K was the most abundant element in all analyzed fruits with an average content of 38770 ± 5590 mg/kg, with a maximum of 46200 mg/kg for Criuleni apples and a minimum of 27270 mg/kg for "Feteasca Neagra" grapes from Purcari. The content of K in the fruits decreased in the following order plum>apple>grape. Calcium, the second major element has a different behavior with an average content of 4370 ± 2800 mg/kg, reaching a maximum value of 8450 mg/kg for the "Feteasca Neagra" grape collected from Purcari vineyard and a minimum of 1110 mg/kg in the case of Cahul apples. Fruits from Criuleni were characterized by a high content of Mg, while its lowest concentration was determined in plums from Cahul. The content of Mg varied between 590 mg/kg and 3000 mg/kg with an average value of 1360 ± 790 mg/kg. Sodium levels in the analyzed fruits were in the range of 211-1820 μg/g and its mean values increased in the following order plum>grape>apple. Chlorine was determined in all fruits, except grape "Feteasca Neagra" from Purcari. The range of its content varied between 120 and 1720 mg/kg, with an average value of 630 ± 500 mg/kg, plums presenting the highest content, and the apple the lowest

Iron had the highest concentration among microelements in all the analyzed fruits followed by Cu and Zn. The highest mean Fe content was determined in grapes followed by apples and plums. Copper levels in the samples ranged from 10 to 41 μg/g with the highest concentration in grape „Merlot" from Purcari. Zinc concentration in the analyzed samples ranged between 3.3 μg/g (apple Cahul) and 43 μg/g (grape "Feteasca Neagra" from Purcari). Manganese's lowest content was determined in the apples from Criuleni (1.6 μg/g) while the highest in grape "Muscat de Hamburg" from Cahul (8.6 μg/g). The mean content of Br in all types of analyzed fruits was on the same level. The highest Ni content (2.03 μg/g) was determined in plums from Criuleni and the lowest in plums from Cahul (0.6 μg/g). The content of Co in analyzed fruits was significantly lower in comparison with other essential elements and lied in the range of 0.025-0.09 μg/g.

Among the selected fruits, the highest concentrations of As were determined in apples from Cahul (0.2 μg/g) and the lowest in grape "Feteasca Neagra" from Purcari (0.036 μg/g). In the grapes „Merlot" from Purcari and all their fruits collected in Criuleni As values were lower than the detection limit of the NAA technique.

In soil samples were determined eight major, rock-forming elements: Na, Mg, Al, Ca, Si, K, Mn, and Fe as well as of 31 trace elements: Sc, Ti, V, Cr, Co, Ni, Zn, As, Br, Rb, Sr, Zr, Mo, Cd, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Hf, Ta, W, Th, and U. The values of *CF* for Mn, Fe, Zn (Purcari), U (Ialoveni and Criulieni) were lower than 1.0 (Table 4.4), indicating that soils were practically uncontaminated by these elements. The values for V, Cr, Zn, As, Cd, Sb, and U lie between 1.0 and 3.0 and point at slight soil pollution. The values obtained for Br indicate moderate pollution by this element. The PLI values were very similar for analyzed zones and indicate moderately to the unpolluted environment.

Table 4.4 The experimental values of *EF*, *CF*, I_{geo}, and *PLI*

	EF				*CF*				*Igeo*			
Element	Purcari	Cahul	Ialoveni	Criuleni	Purcari	Cahul	Ialoveni	Criuleni	Purcari	Cahul	Ialoveni	Criuleni
V	1.36	1.44	1.24	1.40	1.16	1.13	1.19	1.14	-0.37	-0.41	-0.33	-0.39
Cr	1.38	1.48	1.31	1.39	1.18	1.16	1.11	1.14	-0.34	-0.37	-0.44	-0.40
Mn	0.91	1.20	0.97	0.87	0.78	0.94	0.82	0.71	-0.94	-0.67	-0.87	-1.08
Fe	0.81	0.87	0.86	0.84	0.69	0.68	0.73	0.68	-1.11	-1.14	-1.04	-1.13
Co	0.86	0.84	0.84	0.84	0.73	0.66	0.71	0.69	-1.03	-1.18	-1.07	-1.12
Ni	1.06	1.13	1.18	1.15	0.90	0.89	1.00	0.94	-0.73	-0.76	-0.58	-0.67
Zn	1.07	1.62	1.50	1.50	0.92	1.27	1.27	1.22	-0.71	-0.24	-0.24	-0.29
As	2.45	2.50	2.30	2.48	2.10	1.96	1.95	2.03	0.48	0.38	0.38	0.43
Br	9.55	7.89	7.25	7.04	8.19	6.19	6.15	5.75	2.45	2.04	2.03	1.94
Cd	2.44	2.35	2.29	2.81	2.09	1.84	1.94	2.30	0.48	0.30	0.37	0.61
Sb	3.09	3.53	3.30	3.58	2.65	2.77	2.80	2.93	0.82	0.88	0.90	0.96
U	1.40	1.41	1.13	1.22	1.20	1.10	0.96	0.99	-0.32	-0.44	-0.65	-0.59
PLI	**1.39**	**1.38**	**1.37**	**1.36**								

In all analysed fruits the highest values of *TF* were obtained for K, which varied from 1.79 in grape "Feteasca Neagra" from Purcari to 2.9 in plums from Criuleni. In the grapes ”Muscat de Hamburg” and ”Moldova” the *TF* values calculated for Rb were higher or near 1.0. Relatively high values of *TF* were obtained for Ca (0.63), Sr (0.7), and Zn (0.76) in grapes "Feteasca Neagra" from Purcari. For other elements, including elements considered as environmental pollutants, *TF* values were lower than 1.0.

Dairly intake of metal (DIM) and potential HQ values were calculated for seven elements (Co, Fe, Mn, Ni, Zn, As, and Sb), considered as environmental pollutants. The uptake of Co from analyzed fruits was very low. The lowest uptake of Fe was from fruits collected in the Criuleni region, followed by Ialoveni, Purcari, and Cahul regions. Accumulation of Mn changed in the following order grapes>apples>plums, while of zinc in order grapes>plum>apple. Bioaccumulation of toxic elements, As and Sb, from the analyzed fruits, was very low. The HQ values for all elements, except Sb in fruits collected in Criuleni and Cahul regions, were below 1.0, suggesting that analyzed fruits are safe for consumption.

To get more information concerning the similarities as well as the dissimilarities between the investigated fruits the DA was applied (Fig. 4.5). The Root 1 showed a net separation between the apples and plums on one hand and grapes on the other while Root 2 proved the better discrimination between the apples and plums, and a partial overlap between the grapes and apples. From this point of view, Root 1 and Root 2 showed a net difference between plums and apples, and grapes.

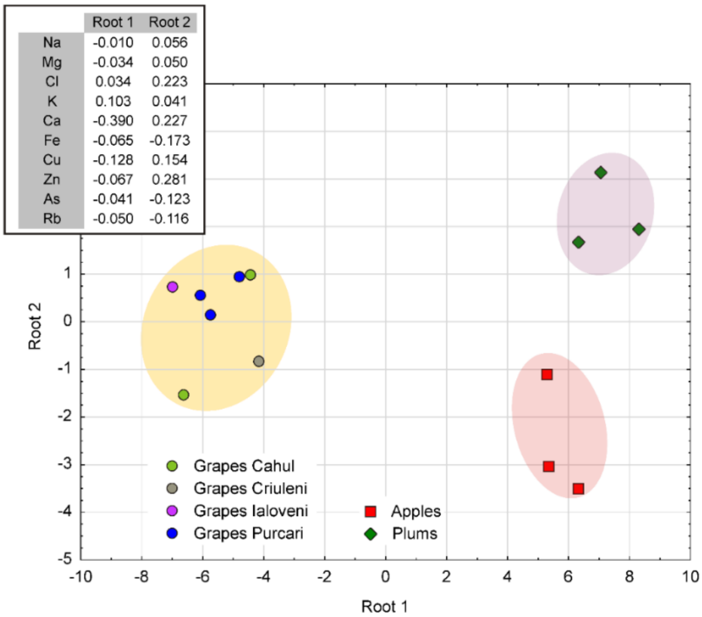

Fig. 4.5 The result of Discriminant Analysis illustrating the existence of three clusters, each of them consisting of a single type of fruits

Further, within the grape cluster, the Purcari vineyard presented the best homogeneity, while the Cahul, Ialoveni, and Purcari showed to be quite different. By analyzing the structure of Root 1 and Root 2, it can be remarked that while in the case of Root 1, only K, Ca and Cu have a relatively significant contribution, in the case of Root 2, the contribution comes from more elements, i,e, Cl, Ca, Fe, Cu, Zn, As and Rb.

4.4 Determination of the elemental composition of medicinal plants of *Lamiaceae* family using NAA

The elemental content of medicinal plants is affected by the geochemical characteristics of soil, application of natural and artificial fertilizers, climatic conditions, vicinity of industry and extensive agricultural activity, and by the ability of herb species to accumulate elements [17,18].

Concentrations of macro and trace elements in 45 species of herbs of *Lamiaceae* family collected in the RM were determined by the mean of NAA. Aerial parts of the plants were collected at the full flowering stage during 2017 from the Experimental subdivision of the Collection of Medicinal Plants of National Botanical Garden (Institute), Moldova

Using NAA, it was possible to determine 26 major and trace elements in analyzed herbs. The content of major elements in analyzed plants changed in the following order K>Ca>Mg>Cl>Na (Fig. 4.6), and were on the level of mg/kg, except Na (µg/g).

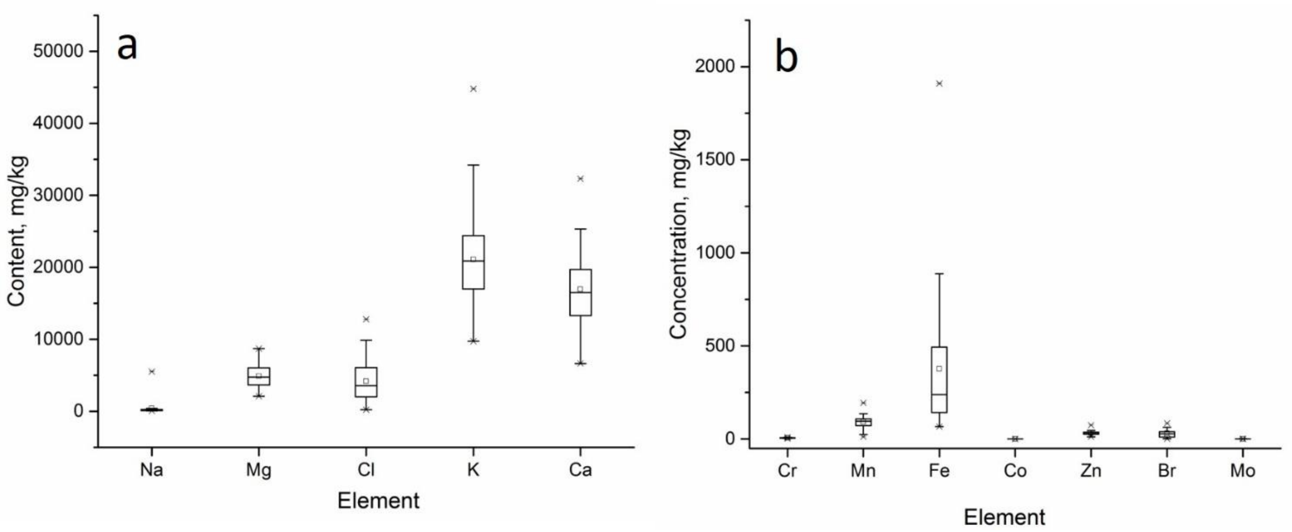

Fig. 4.6 The graphical presentation of (a) macroelements and (b) microelements content in medicinal plant raw materials determined by NAA

The concentration of K in plants ranged from 10700 µg/g in *Melissa officinalis* to 44800 µg/g in the *Lamium album*. Calcium content in analyzed plants varied from 6650 µg/g in *Lavandula angustifolia* to 32300 µg/g in *Nepeta parviflora*. Magnesium lowest content was determined in *Mentha verticillata* (2100 µg/g) and the highest in *Salvia tesquicola* (8710 µg/g). Chlorine content in analyzed plants varied considerably from 208 µg/g in *Salvia sclarea* to 12800 µg/g in *Mentha x gracilis'Variegata'*. Among the major elements, Na concentrations in the plants were the lowest: 44.5 µg/g (*Origanum virens*) - 5530 µg/g (*Mentha x piperita citrata).*

The concentration of essential elements Cr, Mn, Fe, Co, Zn, Mo, and Br determined in the analyzed plants varied significantly (Fig.4.7). Iron was the most abundant microelement in plants, its content varying greatly from 1910 µg/g in *Thymus citriodorus 'Aureus'* plant to 67 µg/g in *Nepeta parviflora*. The zinc level in the analyzed herbs ranged from 13 µg/g (*Scutellaria baicalensis*) to 75 µg/g (*Agastache urticifolia*). Minimal Co concentration was determined in *Nepeta parviflora* (0.03 µg/g) and maximum in *Thymus citriodorus 'Aureus'* (0.88 µg/g). Chromium was detected only in *Ajuga genevensis*, *Origanum vulgare*, *Thymus commosus*, *Thymus vulgare*, and *Mentha x gracilis 'Variegata'* samples. The manganese content in samples ranged from 12.7 µg/g (*Lavandula angustifolia*) to 194 µg/g, with the highest concentration in *Salvia* *verticillate*. Bromine content in samples varied between 2.0 µg/g (*Thymus calcareus*) and 85 µg/g in *Ocimum basilicum* and was lower than the maximum limit established by USP for bromine (< 125 µg/g).

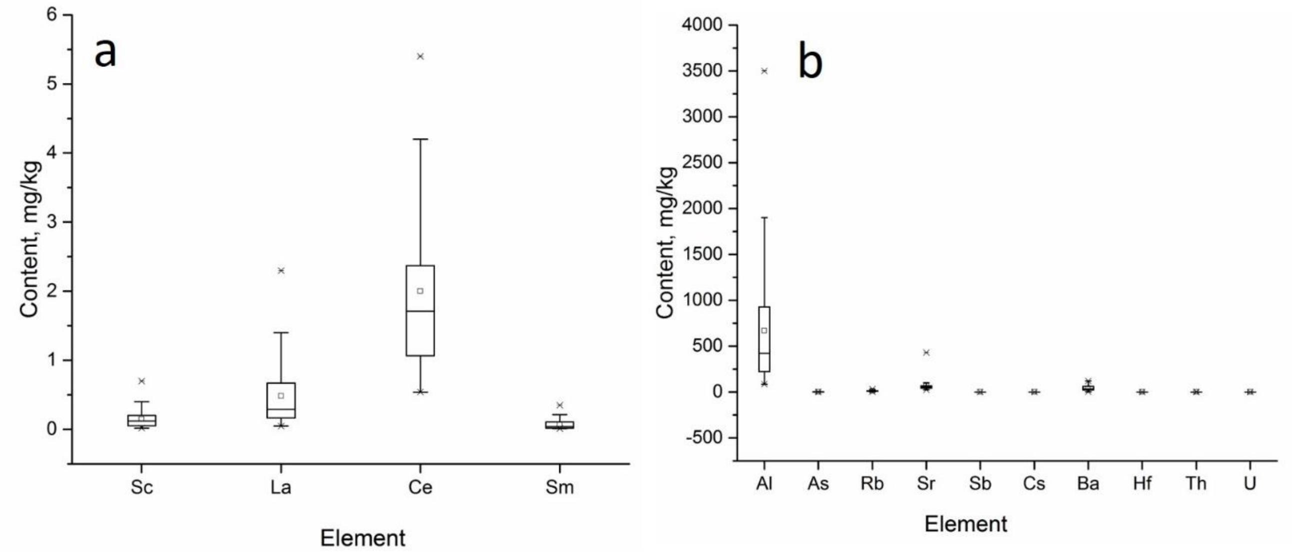

Fig. 4.7 The graphical presentation of (a) rare earth elements and (b) non-essential elements content in medicinal plant raw materials determined by NAA

In medicinal plants from the BG, the content of Sb lied in the range 0.01-0.2 µg/g. Thorium was accumulated by analyzed plants in the range of 0.008-0.75 µg/g and U - 0.005-0.16 µg/g.

Since the medicinal plants are often used as a tee and chemical elements are transferred from plants in tea infusions and further in the human body it is very important to determine the tolerable daily intake (TDI) of potentially toxic elements (Table 4.5).

Table 4.5 Tolerable Daily Intake for elements, considered as potentially toxic

	Element							
	As	Sb	Co	U	Br	Cr	Zn	Mn
	µg/day/person				mg/day/person			
[1]TDI, adult with 70 kg b.w.	6.7	0.3	2.5	0.4	0.3	0.05	0.3	0.9
[2]TDI, adult with 70 kg b.w.	5.3	0.26	2.0	0.36	0.24	0.04	0.25	0.7
TDI value according to WHO	2.1	6	11	0.6	70	0.2	1	3

The calculated TDI values did not exceed the daily intake set by the WHO. The only element, which mean TDI values exceeded permissible level was As. The results obtained revealed that medicinal plants should be carefully used keeping in mind the possible negative impact on human health.

5. ELABORATION OF ENVIRONMENTALLY FRIENDLY SORBENTS FOR WASTEWATER TREATMENT

5.1 Metal removal from the synthetic effluents using *Spirulina platensis*.

Two types of *Spirulina platensis* (*S. platensis)* biomass: one purchased from "Biosolar MSU" company (Moscow, Russia) and the second one obtained from the Institute of Microbiology and Biotechnology (Chisinau, RM) were applied for Ag(I), Pb(II), Ni(II), Zn(II), Cr(III), Cr(VI), and Re(VII) removal from synthetic effluents. Biosorption experiments were conducted varying pH (1.0-6.0), biosorbent dosage (2.0- 20 g/L), initial metal concentration (5-100 mg/L), contact time (3-120 min) and temperature (20-50 ^{0}C). All the experiments were performed in triplicate and the average value of the obtained experimental values was used. Efficiency of metal sorption onto sorbents wad traced using NAA.

pH is one of the most important parameters affecting the biosorption of metal ions, its effect on metal removal efficiency is presented in Fig. 5.1. Maximum lead removal from solution (88-89%) was attained at pH range 3.0-5.0 and of silver at pH 3.0, which corresponds to the removal of 49%. The highest zinc sorption (0.85 mg/g) took place at pH range 4.0- 6.0 and of nickel (760 µg/g) at pH 4.0. Cr(III) maximum removal was attained at pH 3.0 (74%), while pH 2.0 was optimal for Cr(VI) (68%) and rhenium (99%) removal.

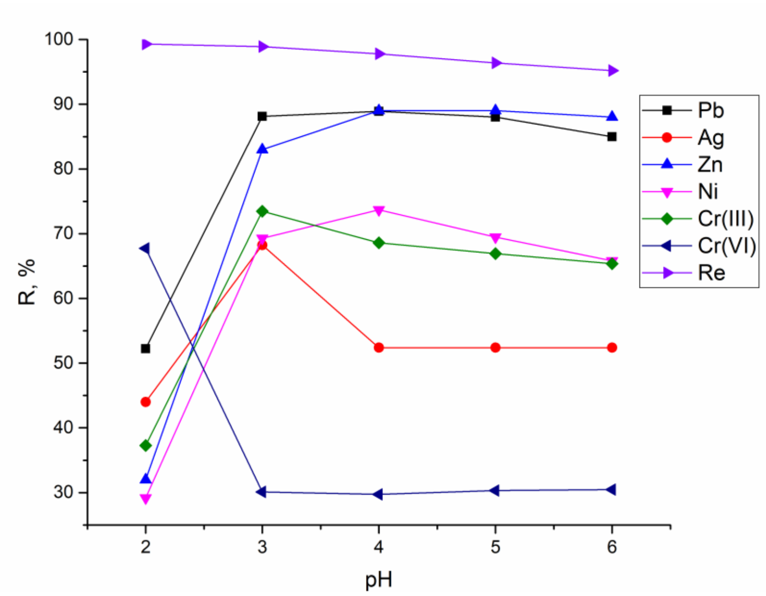

Fig. 5.1 Removal of metal ions at different initial pH (T 20 ^{0}C; C_i 10 mg/L; sorbent dosage 10 g/L; adsorption time 1 h).

With the increase of *S. platensis* concentration from 2 to 20 g/L the percentage of lead adsorbed increased from 54% to 88%, but the equilibrium uptake was decreased from 2.5 to 0.4 mg/g. Maximum sorption of silver ions by *S. platensis* of 14 mg/g was attained at the lowest biosorbent concentration of 2 g. Zinc ions were efficiently removed at all studied sorbent concentrations. Cr(VI) removal efficiency varied from 37% to 67% for the increase of biosorbent concentration from 2 to 14 g/L.

With the increase of initial lead and zinc concentration in solution from 5 to 100 mg/L the *S. platensis* removal capacity increased from 0.23 to 7.24 mg/g for lead and from 0.8 to 4.9 mg/g for zinc. The increase of silver concentration in solution from 5 to 30 mg/L leads to the growth of biomass sorption capacity from 0.8 to 3.7 mg/g. The amount of nickel adsorbed by spirulina biomass was proportional to the initial nickel concentration in the solution, the maximum adsorption capacity being 4.2 mg/g.

The increase of chromium concentration in solution from 10 to 200 mg/L led to the increase of the chromium amount adsorbed by biomass from 1.2 to 11.2 mg/g for Cr(III) and from 0.6 to 9.5 mg/g for Cr(VI). At rhenium concentration in solution 100 mg/L, its content in biomass reached the value of 4.6 mg/g. The experimentally obtained equilibrium data were described using Langmuir, Freundlich, and Temkin equilibrium models. The coefficient of determination (R^2) values indicated that Langmuir and Freundlich models were suitable to describe the biosorption equilibrium for all elements (Table 5.1). Applicability of the two models suggests that the metal ions biosorption by spirulina biomass involves several mechanisms.

Table 5.1 Isotherm parameters for the biosorption of metal ions on *S. platensis* biomass

Element	Isotherm model					
	Freundlich		Temkin		Langmuir	
Pb	R^2	**0.99**	R^2	0.86	R^2	**0.99**
	K_f, mg/g	0.19	a_T, L/g	0.22	q_m, mg/g	11.1
	n	1.25	b_T	1.23	b, L/mg	0.01
Ag	R^2	0.87	R^2	0.82	R^2	**0.98**
	K_f, mg/g	0.15	a_T, L/g	0.23	q_m, mg/g	31.6
	n	1.05	b_T	1.34	b, L/mg	0.004
Zn	R^2	0.94	R^2	0.76	R^2	**0.99**
	K_f, mg/g	0.06	a_T, L/g	0.15	q_m, mg/g	7.1
	n	1.1	b_T	1.81	b, L/mg	0.014
Ni	R^2	**0.99**	R^2	0.86	R^2	**0.99**
	K_f, mg/g	0.1	a_T, L/g	0.17	q_m, mg/g	13.4
	n	1.22	b_T	2.1	b, L/mg	0.006
Cr(III)	R^2	0.95	R^2	0.9	R^2	**0.99**
	K_f, mg/g	0.38	a_T, L/g	0.12	q_m, mg/g	25.0
	n	1.57	b_T	0.78	b, L/mg	0.005
Cr(VI)	R^2	**0.99**	R^2	0.86	R^2	**0.985**
	K_f, mg/g	0.09	a_T, L/g	0.08	q_m, mg/g	16.8
	n	1.13	b_T	0.83	b, L/mg	0.004
Re	R^2	**0.99**	R^2	0.58	R^2	**0.99**
	K_f, mg/g	0.17	a_T, L/g	0.63	q_m, mg/g	142.9
	n	1.02	b_T	0.90	b, L/mg	0.001

Time is important parameter affecting metal biosorption. Maximum lead biosorption was reached after 45 min of sorbent-sorbate interaction, while the optimal time for silver and zinc biosorption can be considered 5 and 30 min, respectively. *S. platensis* biosorption capacity toward nickel ions was increased with increasing of contact time and almost 68% of nickel was removed by biomass in the first 30 min of sorbent-sorbate interaction. The maximum amount of Cr(III) and Cr(VI), was removed in 30 and 45 min of interaction The highest speed of sorption was attained for rhenium, during 1 min 94% of rhenium was removed from the solution.

Four models, namely pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich model (EM), and the intra-particle Weber and Morris diffusion model (IPM), were applied to describe experimental data. The corresponding coefficients of determination values, as well as the kinetic parameters of metal sorption on *S. platensis* biomass, are given in Table 5.2.

Table 5.2 Kinetic parameters for the biosorption of metal ions on *S. platensis* biomass

Element	Kinetic model							
	PFO		PSO		EM		IPM	
Pb	R^2	0.98	R^2	**0.99**	R^2	**-**	R^2	0.39
	q_e, mg/g	0.74	qe, mg/g	0.77	α, mg/g·min	-	k_{diff}	0.07
	k_1, min^{-1}	0.70	k_2, g/mg·min	2.42	β, g/min	-	C_i	0.39
	q_{exp}, mg/g	0.78						
Ag	R^2	**0.99**	R^2	**0.99**	R^2	**-**	R^2	0.31
	q_e, mg/g	2.49	qe, mg/g	2.49	α, mg/g·min	-	k_{diff}	0.17
	k_1, min^{-1}	138	k_2, g/mg·min	4.15	b, L/mg	-	C_i	1.19
	q_{exp}, mg/g	2.5						
Zn	R^2	0.98	R^2	**0.99**	R^2	**-**	R^2	**0.38**
	q_e, mg/g	0.85	qe, mg/g	0.88	α, mg/g·min	-	k_{diff}	0.08
	k_1, min^{-1}	0.85	k_2, g/mg·min	2.59	b, L/mg	-	C_i	0.46
	q_{exp}, mg/g	0.89						
Ni	R^2	0.98	R^2	**0.99**	R^2	**0.99**	R^2	0.5
	q_e, mg/g	0.66	qe, mg/g	0.69	α, mg/g·min	615	k_{diff}	0.07
	k_1, min^{-1}	0.5	k_2, g/mg·min	1.5	b, L/mg	19	C_i	0.23
	q_{exp}, mg/g	0.68						
Cr(III)	R^2	**0.99**	R^2	0.90	R^2	0.98	R^2	0.51
	q_e, mg/g	1.37	qe, mg/g	1.29	α, mg/g·min	315	k_{diff}	0.14
	k_1, min^{-1}	0.43	k_2, g/mg·min	9.73	b, L/mg	8.2	C_i	0.6
	q_{exp}, mg/g	1.41						
Cr(VI)	R^2	0.98	R^2	**0.99**	R^2	**0.99**	R^2	0.5
	q_e, mg/g	0.62	qe, mg/g	0.64	α, mg/g·min	373	k_{diff}	0.06
	k_1, min^{-1}	0.47	k_2, g/mg·min	1.49	b, L/mg	19.9	C_i	0.27
	q_{exp}, mg/g	0.64						
Re	R^2	**1.00**	R^2	**1.00**	R^2	**-**	R^2	0.17
	q_e, mg/g	0.96	qe, mg/g	0.96	α, mg/g·min	-	k_{diff}	0.08
	k_1, min^{-1}	4.6	k_2, g/mg·min	9.39	b, L/mg	-	C_i	0.53
	q_{exp}, mg/g	0.96						

The high values of coefficient of determination (0.99) obtained for the pseudo-second-order and small differences between theoretical and experimental adsorption capacity show this model applicability to describe the experimental for lead, zinc, nickel, and chromium(VI). For chromium(III) the pseudo-first order-model fits better the experimental data, while for silver and rhenium both models were applicable, the differences between $q_{e,exp}$ and $q_{e,cal}$ were insignificant. Elovich model was applicable to describe nickel and chromium (VI) biosorption. For the intra-particle diffusion model, the correlation coefficients were relatively low lying between 0.17 and 0.51.

Industrial effluents are often discharged at relatively high temperatures; thus, the temperature is an important parameter affecting the sorbent biosorption capacity. A maximum lead removal efficiency corresponding to 93% was obtained at the temperature of 30ºC. In case of silver, increase in temperature lead to the decrease of adsorption capacity from 1.74 to 1.20 mg/g. Maximum biosorption of 960 µg Zn/g was obtained at 50 ºC. Increase of temperature had an opposite effect on the biosorption of nickel, Cr(III), and Cr(VI), leading to a decrease of their by biosorption For example, with temperature increase from 20 to 50 °C biomass biosorption capacity for nickel decreased from 883 µg/g to 762 µg/g.

The thermodynamic constants namely, free energy change (ΔG°, kJ/mol), enthalpy change (ΔH°, kJ/mol), and entropy change (ΔS°, J/mol·K) were calculated to evaluate the thermodynamic feasibility of the process and obtained values are presented in Table 5.3.

Table 5.3 Thermodynamic parameters for lead biosorption on *S. platensis*.

Temperature	ΔG	ΔH	ΔS	Temperature	ΔG	ΔH	ΔS
Pb				Ni			
293	-1.53	-0.83	34.8	293	-3.83	3.9	26.4
303	-1.87			303	-4.09		
313	-2.2			313	-4.35		
323	-2.5			323	-4.62		
Ag				Cr(III)			
293	-8.35	-19.24	-37.15	293	-11.24	-11.1	0.35
303	-7.98			303	-11.25		
313	-7.61			313	-11.25		
323	-7.24			323	-11.25		
Zn				Cr(VI)			
293	-10.9	1.33	41.8	293	-9.01	-8.4	2.1
303	-11.3			303	-9.03		
313	-11.7			313	-9.05		
323	-12.1			323	-9.08		

Negative ΔG° values obtained for all the elements showed the spontaneity of the adsorption process. The negative ΔH° value obtained for lead, silver, chromium(III), and chromium(VI) revealed that the adsorption process was exothermic, and for zinc and nickel – endothermic. Silver biosorption by spirulina biomass was predominantly physical, while for the other elements it can be considered as a physicochemical adsorption process.

Metal biosorption includes several processes: metal binding to functional groups, ion-exchange, and microprecipitation. Thus, OH, C=O, and P=O groups can be involved in the lead ions biosorption onto the spirulina biomass. Nickel biosorption was accompanied by the decrease of Na, K, Fe, As, Br, and Sr content in biomass, indicating their possible involvement in the exchange process.

5.2 Metal removal from industrial effluents using biological sorbents

5.2.1 Metal removal from zinc-containing effluents using biological sorbents

Spirulina platensis

The industrial effluent, containing zinc in concentration 45 mg/L (pH 6.5) was taken from the electroplating unit of the "Atom" company, producer of a large volume of construction steel parts, dedicated tanks, and vessels, including those operated under pressure and in aggressive environments. Industrial effluent was collected directly after the electroplating process. From the data presented in Fig. 5.2 it can be seen that the maximum amount of zinc 2.74 mg/g, which corresponds to 61% was adsorbed from effluent by *S. platensis* in 30 min of sorbent sorbate interaction.

To increase the efficiency of zinc removal from effluent the process was studied at biosorbent concentration of 10-60 g/L (Fig. 5.3).

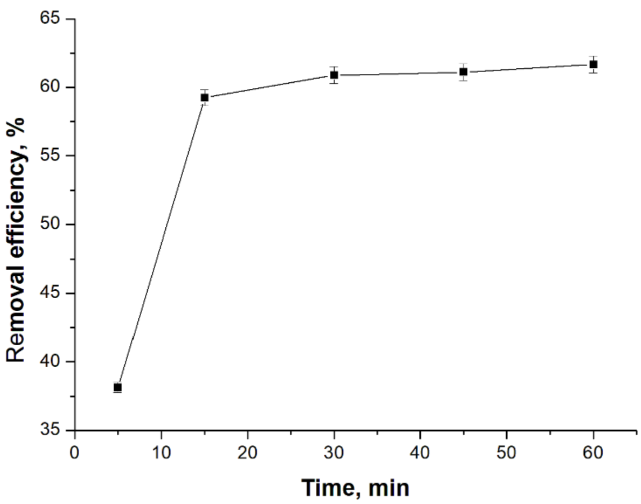

Fig. 5.2 Effect of contact time on the sorption of zinc ions from wastewater by *S. platensis* biomass (T 20 ^{0}C; C_i 45 mg/L; pH 6.5; sorbent concentration 10 g/L).

The increase of biomass concentration resulted in the increase of zinc removal from 61 to 83%. Maximum zinc removal (83%) was achieved at the adsorbent dosage of 60 g/L. However, the difference in biomass removal capacity at sorbent dosage 40 and 60 g/L was just 3%. Therefore, the use of a 40 g/L of biosorbent is justified for economical purposes.

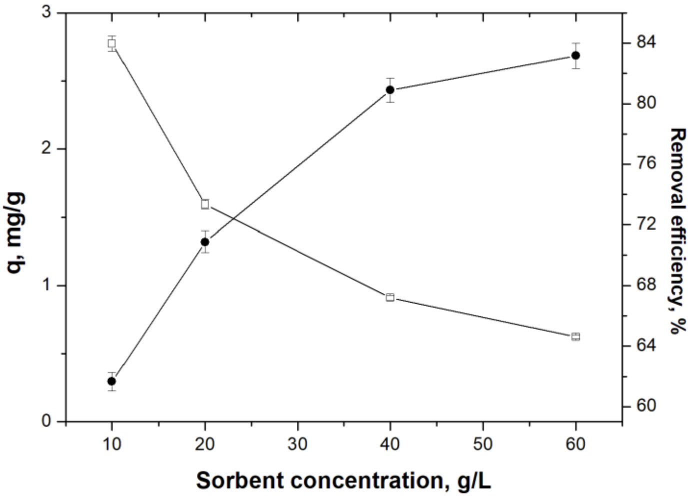

Fig. 5.3 Effect of biosorbent concentrations on biosorption capacity and removal efficiency of zinc ions from wastewater by *S. platensis* biomass (T 20 ^{0}C; C_i 45 mg/L; pH 6.5; adsorption time 1 h).

Saccharomyces cerevisiae

The yeast *Saccharomyces cerevisiae* (*S. cerevisiae*) is one of the economical biosorbents obtained as by-product of fermentation industry. As biosorbent, the yeast *S. cerevisiae* obtained from Efes Vitanta Moldova Brewery (Chisinau, Republic of Moldova) company was used.

In the experiments with *S. cerevisiae* the effluent containing zinc along with the other metal ions was obtained from the same company. Variation of the pH values (2.0-6.0) at sorbent concentrations of 10 g/L allowed reducing concentrations of all elements, except of zinc in the effluent, under the values of maximum permissible concentration (MPC). In order to achive maximum zinc removal the experiment was performed in the subsequent scheme with the addition of new sorbent to the effluent. In the first stage sorbent in the dosages ranging from 20 to 40 g/L was added to 100 mL of effluent at initial effluent pH (6.0). On the second stage, 1.0 g/L or 10 g/L of new biomass were added to the effluent, obtained after the first stage, and shacked for 60 min.

The increase of sorbent concentration on the first stage from 10 to 40 g/L led to a rise of yeast removal capacity from 44 to 72% (Fig. 5.4a). The addition of 1.0 g/L (Fig.5.4b) of new biosorbent to the treated effluent resulted in the removal of 17% of zinc ions in all experimental variants, while the addition of 10 g/L of biosorbent lead to sorption of 47%-52% of zinc onto yeast cells. Therefore, during two cycles it was possible to remove 72-85% of zinc ions from the effluent.

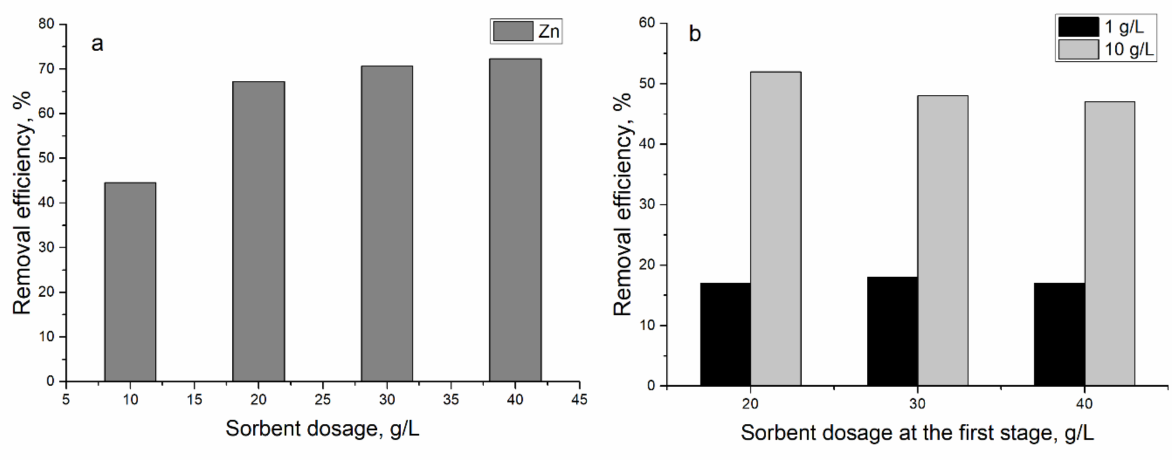

Fig. 5.4 Removal of zinc ions from industrial effluent at different sorbent dosage (at T 20 ºC; adsorption time 1h).

The experiments performed showed that the optimal scheme to achieve the maximal zinc removal is as follows: adding of 20 g/L of yeast biomass on the first stage and 10 g/L on the second stage of treatment.

5.2.2 Metal removal from nickel-containing effluents by biological sorbents

Spirulina platensis

The applicability of *S. platensis* biomass for nickel removal from two types of industrial effluents containing nickel in concentration 14.1 mg/L and 117 mg/L, respectively was investigated. The pH of both effluents was 6.0. Effluents were obtained from electroplating units of the Scientific Production Association "Atom" (Dubna, Russia).

The efficiency of nickel removal from the first effluent was studied using the atomic absorption spectrometry (AAS), while its accumulation in biomass was traced by NAA. The AAS data showed that during 60 min of reaction 66% of nickel was removed from the industrial effluents. Nickel content in biomass increased from 5 μg/g to 625 μg/g (Fig. 5.5).

NAA data showed that besides nickel *S. platensis* biomass removed from wastewater iron, zinc, and barium. Thus, the amount of iron and barium in biomass increased twice in comparison with control, while of zinc – 1.5 times, indicating the possibility of spirulina use for complex wastewater treatment.

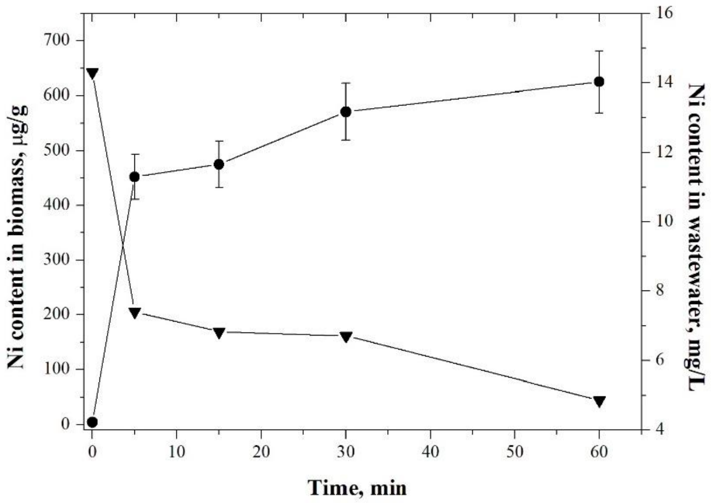

Fig. 5.5 Nickel content in the *S. platensis* biomass and in the industrial effluents versus the (T 20 ^{0}C; C_i 14.1 mg/L; pH 6; adsorption time 1 h).

In the case of the second effluent due to higher nickel concentration, the process of its removal was studied at the dosage range of 6–40 g/L. With the increase of sorbent dosage from 6 to 40 g/L nickel removal efficiency increased from 42 to 68%, however, the increase of sorbent concentration from 20 to 40 g/L resulted in the increase of nickel removal only by 2%. As the nickel concentration in the effluent was relatively high, it is reasonable to treat it firstly in a chemical way to reduce the nickel concentration and after that to apply spirulina biomass for the effluent post-treatment or to use the scheme of subsequent water treatment in several stages with the addition of the new sorbent at each stage.

Saccharomyces cerevisiae

Working with *S. cerevisiae* the nickel-containing effluent, which beside nickel contained other metal ions was obtained from the same company ("Atom"). The metal removal was dependent on the effluent pH. Thus, maximum removal of metals presented in anionic forms molybdenum and chromium was achieved at pH 3.0, 55 and 75%, respectively. Removal of iron and cobalt was also maximal at pH 3.0. Nickel and strontium were better removed at pH 6.0: 42% and 10%, respectively, and zinc at pH 7.0 (52%).

In order to reduce the nickel content in the effluent the subsequent scheme with the addition of new sorbent was applied. At the first stage the increase of biomass concentration from 10 to 40 g/L lead to the rise of nickel removal from 42 to 52%. At the addition of 1.0 g/L of new yeast biomass at the second stage nickel removal constituted 5.7% (first stage 20 g/L), 15% (first stage 30 g/L) and 18% (first stage 40 g/L), thus, the total cumulative removals constituted 54.5%, 66% and 71%, respectively. Addition of 10 g/L of new biomass resulted in the removal of 16% (first stage 20 g/L), 31% (first stage 30 g/L) and 26% (first stage 40 g/L) of nickel ions. Thus, cumulative removal constituted 65%, 82%, and 78%, respectively (Fig. 5.6).

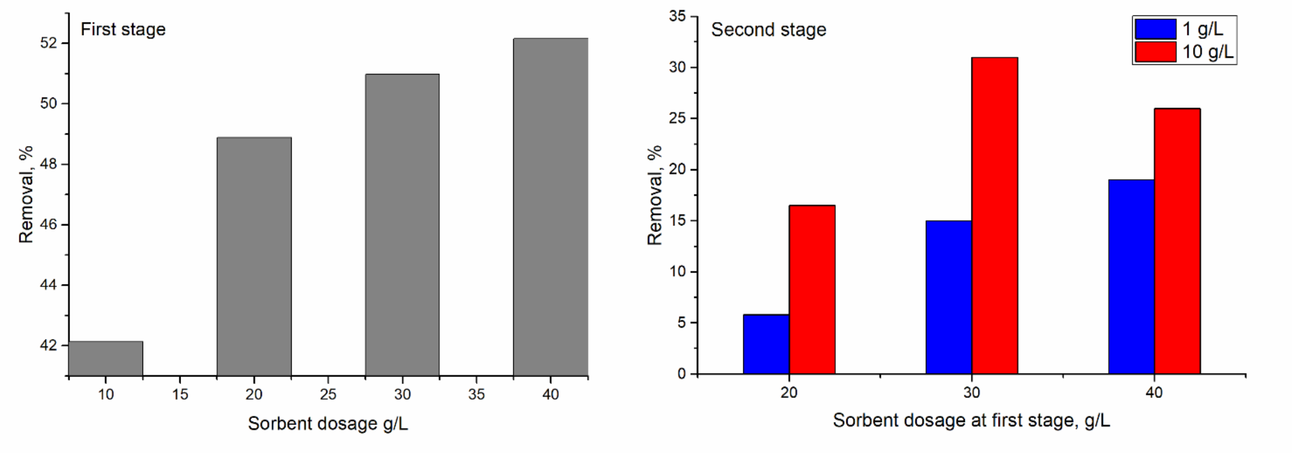

Fig. 5.6 Removal of metal ions from nickel containing effluent at different sorbent dosage (at T 20 ^{0}C; adsorption time 1h)

Shewanella xiamenensis biofilm placed on zeolite

For the treatment of the same effluent *Shewanella xiamenensis* (*S. oneidensis*) biofilm placed on zeolite was used. The removal of nickel from real effluent was very low, 17% at pH 6.0. In order to improve the nickel removal, the amount of biomass was increased from 0.5 to 2.0 g (Figure 5.7). The increase in the biosorbent mass resulted in increased Ni(II) removal, from 17% (sorbent dosage 0.5 g) to 27% (at sorbent dosage 2.0 g). The increase in sorbent dosage four times resulted in a rise in nickel removal only by 10 %.

Since it was shown that applied sorbent is more efficient at low nickel concentrations in solution in the next experiment, the effluent was diluted two and twelve times and 0.5 or 1.0 g of sorbent was added to it. At sorbent dosage of 1.0 g, 26% of Ni(II) was removed from the solution; however, Ni(II) removal after 12-fold dilution amounted to 66% at a sorbent dosage of 0.5 g and 72% at a dosage of 1.0 g (Fig. 5.6c). It can be concluded that *Shewanella xiamenensis* biofilm placed on zeolite can be better used for wastewater post-treatment.

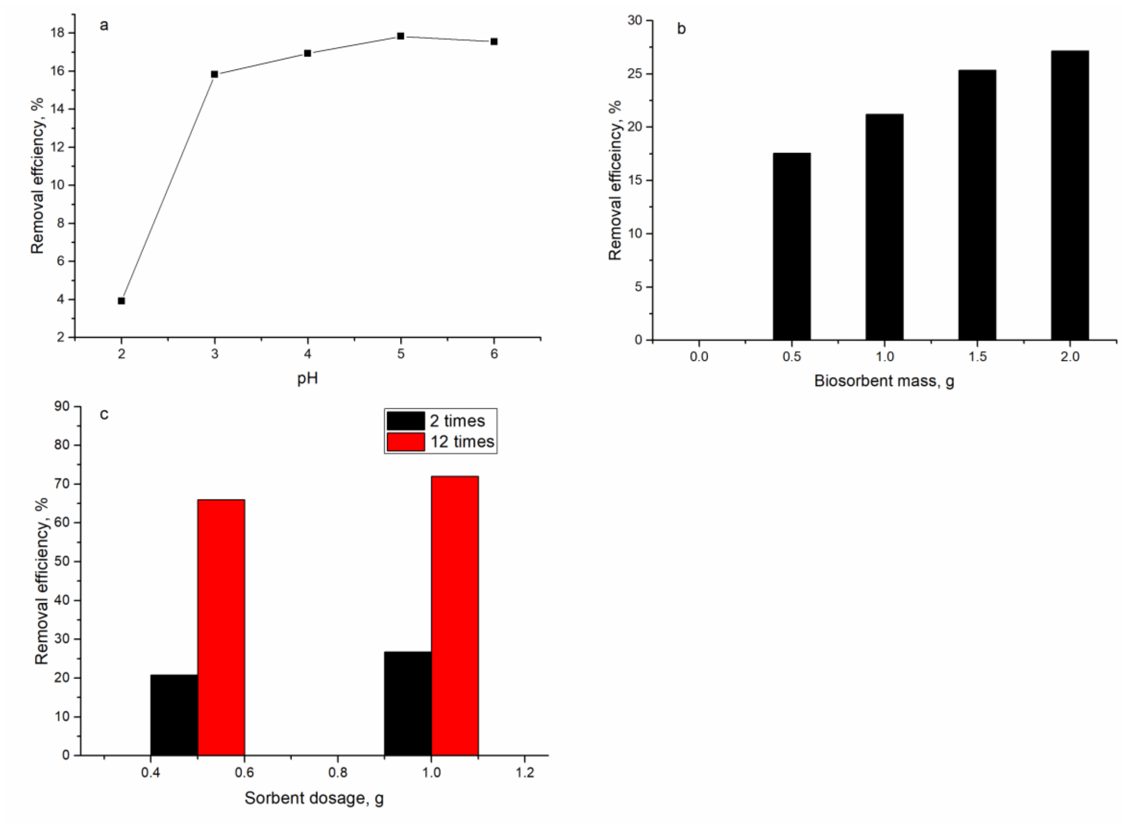

Fig. 5.7 Effect of different parameters on Ni(II) removal from industrial effluent: (a) pH, (b) sorbent dosage (initial effluent), (c) sorbent dosage (diluted effluent).

5.2.3 Metal removal from chromium-containing effluents using biological sorbents

Two types of industrial effluents: the first one containing chromium in concentration 9.4 mg/L, along with other metals such as barium, cobalt, copper, iron, scandium, strontium, and zinc, and the second with chromium concentration of 27 mg/L were obtained from electroplating units of the company “Atom”. Industrial effluents were collected directly after the electroplating process. The pH of both effluents was 4.0.

According to AAS data (Fig. 5.8), the time required for maximal uptake of chromium by *S. platensis* biomass was found to be 15 min.

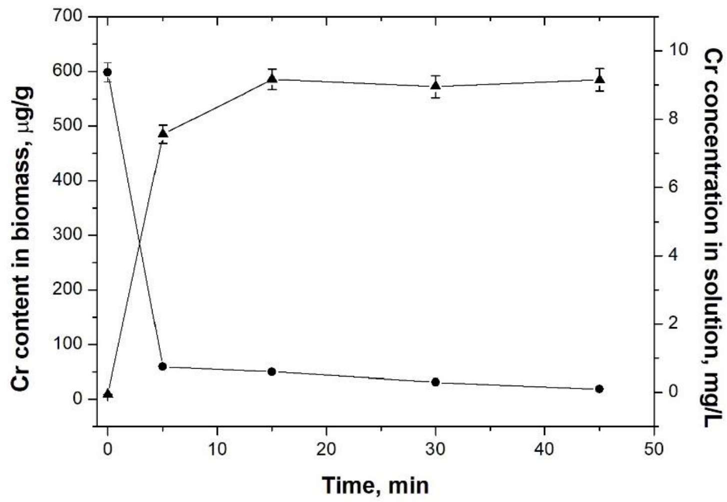

Fig. 5.8 Chromium content in the *S. platensis* biomass and in the industrial effluents versus the contact time biomass (T 20°C; C_0 9.4 mg/L; sorbent concentration 10 g/L, pH 4).

Besides chromium, NAA revealed the uptake of iron, copper, and nickel ions by biomass. In the Cr-loaded biomass, the concentration of iron increased twice and of nickel in 45 times in comparison with the native biomass. The copper content in the native biomass was below the detection limit of its determination, but its concentration achieved the value of 250 μg/g after 45 min of interaction.

5.2.4. Metal removal from rhenium-containing effluents using biological sorbents

Two industrial effluents, containing rhenium were taken from different stages of leaching from polymetallic ore plant (Russia). The data presented in Table 5.4 show that for both effluents *S. platensis* removal rhenium removal efficiency was almost the same - 51-55%. The relatively lower removal capacity of spirulina biomass values obtained for the effluent can be explained by competition of anionic species presented in effluents for binding sites and higher rhenium concentration in comparison with batch solutions.

Table 5.4 The efficiency of rhenium removal from industrial effluents.

	C_i, mg/L	C_f, mg/L	Q, mg/g	Efficiency, %
Effluent I	0.7	0.34	0.069	51
Effluent II	20	8.9	2.23	55

5.2.5 Metal removal from complex effluent

The chemically complex wastewater containing the following metals: Al, Ba, Cr, Fe, Sr, and Zn in different concentrations (pH=6.0) was obtained from electroplating units of the Tactical Missiles Corporation (Dubna, Russia). The data obtained by NAA show that the maximum amount of metals was adsorbed by biomass at the first 5-30 min of spirulina biomass interaction with effluent then the equilibrium was achieved.

During indicated period 100% of barium and 94% of iron was removed from the effluent (Table 5.5). The efficiency of strontium and aluminum removal from effluent was lower 68% and 60%, respectively. Zinc concentration in wastewater decreased by 50%. Although chromium was present in solution in soluble form *S. platensis* showed the lowest removal capacity for this element. The amount of chromium in biomass after one hour of interaction increased approximately fourfold (from 9 to 35 μg/g), however, its removal efficiency was not so high – 37%.

Table 5.5 Amount of metal adsorbed from wastewater at equilibrium time and removal efficiency values

Metal	Concentration of metal remaining in water (C_f), mg/L	q_e, mg/g	R, %
Al	0.08	0.12±0.002	60
Ba	n.d.	0.02±0.001	100
Cr	0.063	0.026±0.001	37
Fe	0.018	2.81±0.08	94
Sr	0.16	0.18±0.005	68
Zn	0.1	0.1±0.002	50

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The results outlined in this thesis support the proposed scientific hypothesis, claiming that the current level of heavy metals in the Republic of Moldova has a negative effect on the quality of the environment and human health, compliment the research in the field of ecological chemistry, and are summarized as follows:

1. Neutron activation analysis proved to be an efficient and highly sensitive technique for the simultaneous determination of considerable number of chemical elements in the environmental samples collected in the Republic of Moldova.
2. Moss biomonitoring techniques (passive and active) applied, for the first time, to assess the quality of air in the Republic of Moldova showed that the main air pollution sources in the country are thermoelectric power plants (V, U, Sb, As), transport (Pb, Zn, Sb, Cu), industrial activity (Fe, Cr, Zn, As, Sb, Br, Ni) and agricultural practice (Cu, As, Sb, Br). The level of air pollution in Moldova can be classified as moderate to severe contaminated environment with the most polluted places being municipalities of Chisinau and Balti.
3. The values of the Hazard Quotient and Hazard Index showed that the emissions of vanadium could negatively affect the human health, especially of children, in the entire country and in Chisinau in particular, and requires special attention of the national authorities.
4. In comparison with the European countries, participating in the moss surveys under the ICP Vegetation programme content of As, Cd, Cr, and Sb in the Republic of Moldova was among the highest, while the concentration of V was the highest.
5. According to neutron activation analysis, the data soils in Moldova can be classified as slightly to moderately polluted with heavy metals. The main contribution to soil pollution with As, Br, and Sb is primarily associated with human activity, namely the intensive use of fertilizers and pesticides.
6. Potassium, followed by Ca and Mg was the dominant element in the analyzed fruits and vine samples. According to the *TF* values, the agricultural crops mainly accumulate these elements from soil. The daily intake values varied greatly depending on the fruit type and place of provenance, while the Hazard index values for Sb in almost all fruit samples were higher than 1.0, indicating that their consumption may present risk for the consumers' health.
7. For the first time, the elemental composition of 45 plant species of the *Lamiaceae* family growing in the Botanical garden in the Republic of Moldova was determined. The analyzed plants were particularly rich in K, Cl, Mg, and Ca. Among the essential elements, Fe was most the abundant, followed by Mn, Zn, Br, Cr, Mo, and Co. In general, metal concentrations in

plants were in line with the literature data, except of As, which concentration in several species exceeded the value established by WHO. Since the tolerable daily intake values for As overpassed the values stated by WHO, this element can constitute threat to human health.

8. Natural water pollution with toxic metals in Moldova as well as the other countries can be reduced through the rigorous industrial and domestic wastewater treatment. The biological sorbents can be considered as excellent alternative to the conventional techniques of metal removal from the wastewater due to their ecological safety, low price, and high efficiency.
9. Three types of biological sorbents (*S. platensis; S. cerevisiae* and bacteria *S. oneidensis* placed on zeolite) were tested for their ability to remove metal ions from synthetic and real, mono- and multi-element effluents. To achieve the maximum metal removal, the effect of different parameters on sorption efficiency of process was investigated. Among the tested biosorbents the yeast *S. cerevisiae* can be regarded as more preferred biosorbent due to its safety, low cost, and possibility to treat complex effluents. *S. platensis* due to its high nutritional value, can be applied as biosorbent only as waste from the different biotechnological processes. Bacteria *S. oneidensis* placed on zeolite is more suitable for the selective metal removal from complex effluents.
10. The results obtained in the thesis are in line with the main objectives of ecological chemistry, allow to expand the area of its application, and contribute for the development of long-lasting approaches of monitoring and prevention of environmental pollution.

Recommendations

11. For the first time the data obtained for the Republic of Moldova were included in the European atlas: "M. Frontasyeva, H. Harmens, A. Uzhinskiy, O. Chaligava and participants of the moss survey (2020). Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. Report of the ICP Vegetation Moss Survey Coordination Centre, Joint Institute for Nuclear Research, Dubna, Russian Federation, 136 p" and could serve as the basis for further moss biomonitoring studies. It is recommended to participate in every five-year moss survey in order to accumulate the data on air pollution with heavy metals in Moldova and to elaborate the legislation which will help to improve the air quality in the country, following the other European countries, for example, Norway.
12. It is recommended to assess the quality of fruits and beverages widely consumed by the population using the modern analytical techniques to determine the concentration of toxic elements. This information will enable to assess the risk of agricultural products consumption on human health and prevent their excessive consumption.

13. It is recommended to apply the biological sorbents for metal removal from wastewater generated by industrial enterprises before their discharge into the natural water bodies. Treatment of wastewater using biological sorbents allows the repeated use of purified water in the technological process thus, reducing clean water consumption and the impact on the environment.

REFERENCES

1. HU, H., JIN, Q., KAVAN, P. A study of heavy metal pollution in China: Current status, pollution-control policies and countermeasures. In*:* *Sustainability*. 2014, nr 6, pp. 5820–5838. ISSN 2071-1050.
2. DUCA, G. Ecological and environmental chemistry. In: *Chemistry Journal of Moldova*. 2017, nr 12, pp. 9–19. ISSN 1857-1727.
3. SARWAR, N., IMRAN, M., SHAHEEN, M.R., ISHAQUE, W., KAMRAN, M.A.; MATLOOB, A., REHIM, A., HUSSAIN, S. Phytoremediation strategies for soils contaminated with heavy metals: Modifications and future perspectives. In: *Chemosphere.* 2017, nr 171, pp. 710–721. ISSN 1879-1298.
4. PACYNA, E.G., PACYNA, J.M., FUDALA, J., STRZELECKA-JASTRZAB, E., HLAWICZKA, S., PANASIUK, D., NITTER, S., PREGGER, T., PFEIFFER, H., FRIEDRICH, R. Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. In: *Atmospheric Environment*. 2007, nr 41, pp. 8557–8566. ISSN 1352-2310.
5. *World Health Organization, European Centre for Environment and Health. UN Bonn*, ©2020, [accessed on May 12, 2020]. Available: https://www.unbonn.org/WHO-ECEH.
6. LI, C., ZHOU, K., QIN, W., TIAN, C., QI, M., YAN, X., HAN, W. A Review on Heavy Metals Contamination in Soil: Effects, Sources, and Remediation Techniques. In: *Soil and Sediment Contamination*. 2019, nr 28, pp. 380–394. ISSN 1532-0383
7. MUDU, P., TERRACIN, B., MARTUZZI, M. Human Health in Areas with Industrial Contamination. Denmark:WHO Regional Office for Europe, 2014 [accessed on May 20, 2020]. Available: https://apps.who.int/iris/bitstream/handle/10665/144490/9789289050050-eng.pdf?sequence=1&isAllowed=y;
8. CRIVOI, A., AVASĬLOAEl, I. Evaluarea calităţii aerului atmosferic din spaţiile verzi ale municipiului Chişinău. In: Revistă ştiinţifică, de educaţie, spiritualitate şi cultură ecologică. 2014, nr 10, pp. 119-125. ISSN 1857-3517
9. *State of The Environment Report 2004*. Chişinău: Ministry of Ecology and Natural Resources. National Institute of Ecology Republic of Moldova, 2005. ISBN 9975-9642-3-

0.10.

10 GUPTA, N., YADAV, K.K., KUMAR, V., KUMAR, S., CHADD, R.P., KUMAR, A. Trace elements in soil-vegetables interface: Translocation, bioaccumulation, toxicity and amelioration - A review. In*: Science of the Total Environment*. 2019, nr 651, pp. 2927–2942. ISSN 0048-9697.

11. DING, Z., LI, Y., SUN, Q., ZHANG, H. Trace elements in soils and selected agricultural plants in the tongling mining area of China. In: *International Journal of Environmental Research and Public Health.* 2018, nr 15(2), pp. 202. ISSN 1660-4601.

12. CLRTAP *Mapping of Effects on Materials, Chapter IV of Manual on methodologies and criteria for modelling and mapping critical loads and levels and air pollution effects, risks and trends*; 2014;

13. JIGAU, G., MOTELICA, M., LESANU, M., TOFAN, E., GEORGESCU, L., ITICESCU, C., ROGUT, V., NEDEALCOV, S. Heavy Metals in the Anthropogenic Cycle of Elements. In: *Soil as World Heritage*, Springer Netherlands. 2014, pp. 61–68. ISBN: 9789400761872.

14. *Monitorul Oficial 303-bis din 06 Noiembrie 1997*, ©1997. [accessed on May 25, 2020)]. Available: http://www.monitoruljuridic.ro/monitorul-oficial/303-bis/1997-11-06/

15. *Тяжелые металлы в почве, ПДК, ОДК.* ©2020. [accessed on May 25, 2020)]. Available: http://www.gidrogel.ru/ecol/hv_met.htm#table2

16. OIV *International Oenological codex*; 2011;

17. PYTLAKOWSKA, K., KITA, A., JANOSKA, P., POŁOWNIAK, M., KOZIK, V. Multi-element analysis of mineral and trace elements in medicinal herbs and their infusions. In: *Food Chemistry.* 2012, nr 135, pp. 494–501. ISSN 0308-81446.

18. JURANOVIĆ CINDRIĆ, I., ZEINER, M., GLAMUZINA, E., STINGEDER, G. Elemental characterisation of the medical herbs Salvia officinalis L. and Teucrium montanum L. grown in Croatia. In: *Microchemical Journal.* 2013, nr 107, pp. 185–189. ISSN 0026-265X.

LIST OF PUBLICATIONS ON THE SUBJECT OF THE THESIS

Monographs

1. **ZINICOVSCAIA, Inga**, CEPOI, Liliana. *Cyanobacteria for Bioremediation of Wastewaters.* Springer International Publishing, 2016, 124 p. ISBN: 978-3-319-26749-4.
2. **ЗИНЬКОВСКАЯ, Инга**. *Взаимодействие микроводорослей с металлами на примере Arthrospira (Spirulina) platensis.* Москва: Издательство «Перо», 2017. 33 с. ISBN 978-5-907016-65-1.

Chapters in books

3. **ZINICOVSCAIA, Inga**, YUSHIN, Nikita, VEGEL, Konstantin, GROZDOV, Dmitrii. Moss Biomonitoring in Former Sovet Union Countries: A Review. In: Gheorghe DUCA, Ashok VASEASHTA, eds. *Emerging Developments and Environmental Impacts of Ecological Chemistry*. GI Global, 2020, pp. 511-529. SBN13: 9781799812418.
4. CEPOI, Liliana, **ZINICOVSCAIA, I**nga. *Spirulina platensis* as a model object for the environment bioremediation studies. In: Ozcan KONUR ed. *The Handbook of Algal Science, Microbiology, Technology, and Medicine*. London:Academic Press, 2020, pp. 629-638. SBN13 978-0128183052
5. **ZINICOVSCAIA, Inga**. Biosorption of trace elements. In: Katarzyna CHOJNACKA, Agnieszka SAEID eds. *Recent advances in trace elements: chemistry, biology, biomedicine and environment.* Wiley-Blackwell, 2018, pp. 235-250. ISBN: 978-1-119-13379-7.
6. **ZINICOVSCAIA, Inga, FRONTASYEVA, Marina**. Moldova. In: Marina FRONTASYEVA, Harry HARMENS, Alexander UZHINSKIY, Omari CHALIGAVA and participants of the moss survey (2020). *Mosses as biomonitors of air pollution: 2015/2016 survey on heavy metals, nitrogen and POPs in Europe and beyond. Report of the ICP Vegetation Moss Survey Coordination Centr*e. Dubna: Joint Institute for Nuclear Research, 220, pp. 96-97. ISBN 978-5-9530-0508-1.

Articles

7. **ZINICOVSCAIA, I.**, HRAMCO, C., DULIU, O.G., VERGEL, K., CULICOV, O.A, FRONTASYEVA M.V., DUCA, GH. Air pollution study in the Republic of Moldova using moss biomonitoring technique. In: *Bulletin of Environmental Contamination and Toxicology*. 2017, vol. 98, nr. 2, pp. 262-269. ISSN 1432-0800.
8. **ZINICOVSCAIA, I.**, ANIČIĆ UROŠEVIĆ, M., VERGEL, K., VIERU, E., FRONTASYEVA, M., POVAR, I., DUCA, GH. Active moss biomonitoring of trace elements with *Sphagnum girgensohnii* in relation to atmospheric bulk deposition: Chisinau case study. In: *Ecological Chemistry and Engineering S*. 2018, vol. 25, nr. 3, pp. 361-372. ISSN 2084-4549.
9. STURZA, R., BILICI, C., **ZINICOVSCAIA, I.**, CULICOV, O.A., GUNDORINA, S.F., DUCA, GH. Determination of eight elements in Moldovian wine using ICP-MS and NAA. In: *Revue Roumaine de Chimie*. 2015, vol. 60, nr. 11-12, pp.1065-1071. ISSN 0035-3930.
10. **ZINICOVSCAIA, I.**, DULIU, O.G., CULICOV, O. A., FRONTASYEVA, M., STURZA, R. Major and trace element distribution in soil of two Moldavian vineyards: Romanesti and Cricova. In: *Romanian Reports in Physics*, 2018, vol. 70, p. 701. ISSN 1841-8759.

11. **ZINICOVSCAIA, I.**, DULIU, O.G., CULICOV, O., STURZA, R., BILICI, C., GUNDORINA, S. Geographical origin identification of Moldavian wines by neutron activation analysis. In: *Food Analytical Methods*. 2017, vol. 10, pp. 3523–3530. ISSN: 1936-9751.

12. **I. ZINICOVSCAIA,** R. STURZA, O. G. DULIU, D. GROZDOV, S. GUNDORINA, A. GHENDOV-MOSANU, GH. DUCA. Determination of major and minor elements in Moldavan fruits by neutron activation analysis and assessment of their provenance. In: *International Journal of Environmental Research and Public Health*. 2020, vol. 17, p.7112; ISSN 1660-4601.

13. **ZINICOVSCAIA, I.**, STURZA, R., GURMEZA, I., VERGEL, K., GUNDORINA, S., DUCA, GH. Metal bioaccumulation in the soil-leaf-fruit system determined by neutron activation analysis. In*: Journal of Food Measurement and Characterization*. 2019, vol. 13, nr. 1, pp. 592-601. ISSN 2193-4134.

14. **I. ZINICOVSCAIA**, S. GUNDORINA, K. VERGEL, D. GROZDOV, A. CIOCARLAN, A. ARICU, I. DRAGALIN, N. CIOCARLAN. Elemental analysis of *Lamiaceae* medicinal and aromatic plants growing in the Republic of Moldova using neutron activation analysis. In: *Phytochemistry Letters*. 2020, vol. 35, pp. 119-127. ISSN 1874-3900.

15. CEPOI, L., **ZINICOVSCAIA, I.**, RUDI, L., CHIRIAC, T., MISCU, V., DJUR, S., STRELKOVA, L., VERGEL, K., NEKHOROSHKOV, P. Growth and heavy metals accumulation by *Spirulina platensis* biomass from multicomponent copper containing synthetic effluents during repeated cultivation cycles. In: *Ecological Engineering*. 2020, vol.142, pp. 105637. ISSN 0925-8574.

16. **ZINICOVSCAIA, I.**, YUSHIN, N., SHVETSOVA, M., FRONTASYEVA, M. Zinc removal from model solution and wastewater by Spirulina platensis biomass. In: *International Journal of Phytoremediation*. 2018, vol. 20, nr. 9, pp. 901-908. ISSN 1549-7879.

17. **ZINICOVSCAIA, I.**, SAFONOV, A., TROSHKINA, I., ILIN, V., DEMINA, L., GERMAN, K. Biosorption of Re(VII) from aqueous solutions by cyanobacteria *Spirulina platensis*. In: *CLEAN - Soil, Air, Water*. 2018, vol. 46, nr. 7, pp. 1700576, ISSN 1863-0669.

18. **ZINICOVSCAIA, I.**, YUSHIN, N., RODLOVSKAYA, E., KAMANINA, I. Biosorption of lead ions by cyanobacteria *Spirulina platensis*: kinetics, equilibrium and thermodynamic study. In: *Nova Biotechnologica et Chimica*. 2017, vol. 16, nr. 2, pp.105-112. ISSN 1338-6905.

19. **ZINICOVSCAIA, I.**, CEPOI, L., CHIRIAC, T., MITINA, T., D. GROZDOV, N. YUSHIN, O. CULICOV. Application of *Arthrospira (spirulina) platensis* biomass for silver removal from aqueous solutions. In: *International Journal of Phytoremediation*. 2017, vol. 19, nr. 11, pp. 1053-1058, ISSN 1549-7879.

20. YUSHIN, N., **ZINICOVSCAIA, I.**, CEPOI, L., CHIRIAC, T., MITINA, T., DUCA, GH. Study of chemistry of Cr(VI)/C(III) biosorption from batch solutions and electroplating industrial effluent using cyanobacteria Spirulina platensis. In: *Revue Roumaine de Chimie,* 2018, vol. 64, nr. 2, pp. 173-181. ISSN 0035-3930.

21. **ZINICOVSCAIA, I.**, YUSHIN, N., GUNDORINA, S., DEMČÁK, Š., FRONTASYEVA, M., KAMANINA, I. Biosorption of nickel from model solutions and electroplating industrial effluent using cyanobacteria *Spirulina platensis*. In: *Desalination and Water Treatment*. 2018, vol. 120, pp. 158-165**.** ISSN 1944-3986.

22. ДУКА, Г., **ЗИНЬКОВСКАЯ, И.,** ГРОЗДОВ, Д. Биосорбция ионов металлов микроводорослью *Spirulina plantensis*. In: *Экологическая химия*. 2020, vol. 29, nr. 1, pp. 28–35. ISSN 0869-3498.

23. **ZINICOVSCAIA, I.,** YUSHIN, N., GROZDOV, D., VERGEL, K., POPOVA, N., ARTEMIEV, G., SAFONOV A. Metal Removal from Nickel-Containing Effluents Using Mineral–Organic Hybrid Adsorbent. In: *Materials*. 2020, vol. 13, nr.19, pp. 4462. ISSN 1996-1944.

24. **ZINICOVSCAIA, I.**, YUSHIN, N., GROZDOV, D., BOLDYREV, K., RODLOVSKAYA, E., OSTROVNAYA, T. Metal removal from synthetic and real galvanic nickel – containing effluents by *Saccharomyces cerevisiae*. In: *Chemistry and Ecology*. **2021**, vol. 37, nr.1, pp. 83-103. ISSN 0275-7540.

25. **ZINICOVSCAIA, I.**, YUSHIN, N., ABDUSAMADZODA, D., GROZDOV, D., SHVETSOVA, M. Efficient Removal of Metals from Synthetic and Real Galvanic Zinc–Containing Effluents by Brewer's Yeast *Saccharomyces cerevisiae*. In*: Materials*. **2020**, vol. 13, pp. 3624. ISSN 1996-1944.

26. **ZINICOVSCAIA I.**, GROZDOV D., YUSHIN N., ABDUSAMADZODA D., GUNDORINA S.F., RODLOVSKAYA E., KRISTAVCHUK O. Metal removal from chromium containing effluents by *Saccharomyces cerevisiae*. In: *Desalination and Water Treatment*. 2020, vol. 178, pp.:254-270. ISSN 1944-3986.

27. **ZINICOVSCAIA, I.**, SAFONOV, A., BOLDYREV, K., GUNDORINA, S., YUSHIN, N., PETUHOV. O., POPOVA, N. Selective metal removal from chromium-containing synthetic effluents using *Shewanella xiamenensis* biofilm supported on zeolite. In: *Environmental Science and Pollution Research*. 2020, vol. 27, pp. 10495–10505. ISSN 0944-1344.

28. **ZINICOVSCAIA, I.**, CEPOI, L., CHIRIAC, T., RUDI, L., CULICOV, O.A., FRONTASYEVA, M.V., PAVLOV, S., KIRKESALI, E., GUNDORINA, S., MITINA, T., AKSHINTSEV, A., RODLOVSKAYA, E. *Spirulina platensis* as biosorbent of chromium and nickel from wastewaters. In: *Desalination and Water Treatment*. 2016, vol. 57, nr. 24, pp. 11103-11110. ISSN 1944-3986.

29. **ZINICOVSCAIA, I.**, L. CEPOI, I. POVAR, T. CHIRIAC, E. RODLOVSKAYA, O.A. CULICOV. Metal uptake from complex industrial effluents by *Spirulina platensis* using neutron activation analysis. In: *Water, Air, & Soil Pollution* 2018, vol. 229, nr. 7, 220. ISSN 0049-6979.

30. **ZINICOVSCAIA, I.** Removal of chromium from wastewater by activated carbon and *Spirulina platensis*: a comparative study. In: Journal of Science and Arts. 2015, vol. 3, nr. 32, pp. 239-248. ISSN 1844-9581.

Conference paper

31. **ZINICOVSCAIA, Inga.** Management of the Quality of the Air in the Republic of Moldova Based on the Moss Biomonitoring Data. In: *Proceedings of the Fourteenth International Conference on Management Science and Engineering Management*, July 31 - August 1st. 2020, Chisinau, Moldova, Springer International Publishing, 2021, pp .311-325, ISBN 978-3-030-49888-7.

ANNOTATION

Zinicovscaia Inga, Impact of some metals determined by neutron activation analysis on the quality of the environment. Thesis of doctor habilitate in chemistry, Chisinau, 2022

Structure of the thesis: Annotation (English, Romanian, Russian), Introduction, Five Chapters, Conclusions and Recommendations, Bibliography of 506 titles, 66 figures, 45 tables, and 212 pages of basic texts. The results of the thesis were published in 50 papers, including 24 articles with impact factor, 2 books and 4 book chapters.

Field of research: 145.01. Ecological Chemistry

Keywords: metals, neutron activation analysis, passive biomonitoring, active biomonitoring, soil, pollution, agricultural crops, elemental content, transfer factor, wastewater treatment, biosorption.

The scope and objectives of the thesis: The main objective of the thesis is the analysis of the content of some chemical elements using neutron activation analysis in order to determine the biological value of the environment, to assess the risk on human health and state of ecological systems, as well as to develop the technology of metals removal from industrial effluents using different types of sorbents.

The novelty and scientific originality: For the first time in the Republic of Moldova neutron activation analysis was used to determine the content of elements in mosses, soils, fruits, vines, medicinal plants. The originality of the thesis consists in the simultaneous determination of a considerable number of chemical elements and estimation of the state the environment on the basis of these data. The technology of metal removal from mono- and multicomponent systems was proposed.

The obtained result, which contributes to the creation of the new scientific direction: Application of neutron activation analysis in estimation of the biological value of the habitat for life based on the determination of the elemental composition of the different environmental samples.

The theoretical importance of the work. A new theoretical and practical approach in the field of ecological chemistry has been proposed, which allow based on the chemical composition evaluation of the non-carcinogenic risk, calculation of hazard coefficient for air, soil, agricultural crops polluted with metals and the values of transfer factor in soil-agricultural crops systems. The optimal physico-chemical conditions for metals maximum removal using different types of biological sorbents have been established.

The applied value of the work. The inclusion of the results of the biomonitoring study of air pollution in the Republic of Moldova in the „European Atlas of Heavy Metal Atmospheric Deposition" edited by „ICP Vegetation Programme Coordination Center" indicate the value of ang high appreciation of the performed research. Determination of the elemental composition of fruits, wines, and medicinal plants is extremely important for the assessment of their quality and effect on the consumers' health as well as identification of their origin. The results obtained for different sorbents can be used for the elaboration of the methods of metals removal with the purpose to reduce their concentration to maximum admissible levels.

The implementation of the results: The obtained results can be implemented in the training of the local producers of medicinal and aromatic plants, for analysis of the agricultural products and for the development of the new technique of metal removal using biological sorbents. The results were implemented at Public Institution "Central laboratory for testing alcoholic/non-alcoholic beverages and canned goods", Moldovan Association of Aromatic and Medicinal Plant Producers "AROMEDA", Institute of Chemistry, and Institute of Microbiology and Biotechnology, Chisinau, Republic of Moldova.

ADNOTARE

Zinicovscaia Inga, Impactul unor metale determinate prin analiza de activare cu neutroni asupra calitații mediului ambiant, Teză de doctor habilitat în științe chimice, Chișinău, 2022

Structura tezei: Adnotare (în engleză, română şi rusă), Introducere, Cinci capitole, Concluzii si recomandări, Bibliografie cu 506 surse, 66 figuri, 45 tabele, 212 pagini de text. Rezultatele obţinute au fost publicate în 50 lucrări ştiinţifice, inclusiv 24 articole cu factor de impact, 2 monografii si 4 capitole în cărți.

Domeniul de studii: 145.01. Chimie ecologică

Cuvintele-cheie: metale, analiza prin activare cu neutron, biomonitoring pasiv, biomonitoring activ, sol, poluarea, culturile agricole, compoziția elementală, factor de transfer, tratarea apelor reziduale, biosorbția.

Scopul şi obiectivele tezei: Obiectivul principal al tezei este analiza conţinutului unor elemente chimice prin metoda de activare cu neutroni cu scopul determinării valorii biologice a mediului ambiant, evaluarii riscului asupra sănătății și stării sistemelor ecologice, precum și elaborarea tehnologiei de indepărtare a metalelor din apele industriale folosind diferite tipuri de sorbenți.

Noutatea şi originalitatea ştiinţifică: Pentru prima data în Republica Moldova a fost folosită analiza prin activare cu neutroni pentru evaluarea conținutului de elemente chimice în muschi, soluri, fructe, vinuri, plante medicinale. Originalitatea lucrării constă în determinarea simultană a unui numar considerabil de elemente chimice și evaluarea pe baza aceestor date a stării mediului ambiant. A fost propusa tehnologia de indepărtare a metalelor din sistemele mono- și multicomponente.

Rezultatele obținute care au determinat crearea unei noi direcţii ştiinţifice: Aplicarea analizei de activare prin neutroni în estimarea valorii habitatului pentru viață în baza determinarii compoziției chimice a diferitor obiecte din mediu.

Semnificaţia teoretică a tezei: A fost propusă o noua abordare teoretică și practică în domeniul chimiei ecologice pentru analiza chimica a mediului ambiant, care permite pe baza compozitiei elementale evaluarea riscului non-cancerogenic, calculul coeficientului de pericol pentru aer, soil, culturile agricole poluate cu metalele; si factorului de transfer a elementelor chimice în sisteme sol-culturile agricole. Au fost stabilite condițiile fizico-chimice optime pentru indepărtarea maxima a metalelor folosind diferite tipuri de sorbenți biologici.

Valoarea aplicativă a tezei. Includerea rezultatelor biomonitoringului poluării aerului din Republica Moldova în „European Atlas of Heavy Metal Atmospheric Deposition" editat de „ICP Vegetation Programme Coordination Center" susține valoarea și aprecierea înaltă a cercetărilor efectuate. Determinarea compozitiei elementale a fructelor, vinurilor, plantelor medicinale este extrem de importantă pentru estimarea calitatii lor și impactului asupra sănătății consumatorilor, precum și stabilirea provenineței lor; rezultatele obținute pentru diferiți sorbenți pot fi folosiți pentru elaborarea metodelor de îndepărtare a metalelor cu scopul de a reduce concentrațiile lor la limitele maxim admisibile.

Implementarea rezultatelor ştiinţifice: Rezultatele obținute pot fi implementate în procesul de instruire a producătorilor locali de plante medicinale și aromatice, pentru analiza produselor agricole și pentru elaborarea metodelor de îndepărtare a metalelor grele din apele uzate. Rezultatele au fost implementate la Instituţia Publică „Laboratorul central de testare a băuturilor alcoolice/nealcoolice şi a produselor conservate", Asociaţia Cultivatorilor de Plante Aromatice şi Medicinale din Republica Moldova "AROMEDA", Institutul de Chimie, Institutul de Microbiologie si Biotechnologie, or. Chișinău, Republica Moldova.

АННОТАЦИЯ

Зиньковская Инга, Влияние некоторых элементов, определенных методом нейтронного активационного анализа на качество окружающей среды, диссертация доктора химических наук, Кишинев, 2022

Структура диссертации: Аннотация (на английском, румынском и русском языках), введение, пять глав, выводы и рекомендации, библиография из 506 источников, 66 рисунков, 45 таблиц и 212 страниц основного текста. Результаты диссертации отражены в 50 научных публикациях, включая 24 статьи в реферируемых журналах, 2 монографии и 4 главы в книгах.

Область исследования: 145.01. экологическая химия

Ключевые слова: металлы, нейтронно-активационный анализ, активный биомониторинг, пассивный биомониторинг, почвы, загрязнение, сельскохозяйственные культуры, фактор переноса, элементный анализ, очистка сточных вод, биосорбция.

Цель и задачи работы: основной целью диссертации является определение содержания ряда химических элементов методом нейтронно-активационного анализа в природных образцах для биологической оценки состояния окружающей среды; оценка риска для здоровья человека и состояния экологических систем; а также, разработка технологии извлечения металлов из промышленных сточных вод, используя различные типы сорбентов.

Научная новизна и оригинальность исследования: впервые в Республике Молдова нейтронно-активационный анализ был применен для определения содержания химических элементов во мхах, почвах, фруктах, винах и медицинских растениях. Оригинальность работы заключается в одновременном определении значительного количества химических элементов и оценке, на основе этих данных, состояния окружающей среды. Была предложена технология извлечения металов из моно- и многокомпонентных систем.

Полученные результаты, которые определили развитие нового научного направления: применение нейтронно-активационного анализа для оценки качества естественной среды обитания на основе определения элементного состава различных объектов окружающей среды.

Теоретическая значимость работы. Были предложены новые теоретические и практические подходы в области экологической химии, которые позволяют, на основе элементного состава образцов, оценить риски для здоровья человека, рассчитать значения коэффициента опасности загрязнения воздуха, почвы, сельскохозяйственных культур металлами; а также значения фактора переноса элементов в системах почва-сельскохозяйственные культуры. Были установлены оптимальные физико-химические параметры для максимального извлечения ионов металлов различными типами биологических сорбентов.

Практическая значимость работы. Включение результатов по оценке качества воздуха в Республике Молдова в „European Atlas of Heavy Metal Atmospheric Deposition” издаваемый „ICP Vegetation Programme Coordination Center” указывает на значимость и высокую оценку проведенных исследований. Определение элементного состава фруктов, вин, медицинских растений критически важно для оценки их качества и влияния на здоровье потребителей, а также определения их происхождения. Результаты, полученные для разных сорбентов, могут быть использованы для разработки методов извлечения металлов из сточных вод с целью снижения их концентраций до уровня ПДК.

Внедрение полученных результатов: Полученные результаты могут быть использованы для инструктирования местных производителей медицинских и ароматических растений, для анализа качества сельскохозяйственной продукции и для разработки новых методов извлечения металлов из промышленных сточных вод, используя биологические сорбенты. Полученные результаты были применены в Центральной испытательной лаборатории тестирования алкогольных/безалкогольных напитков и консервов, Ассоциации производителей ароматических и медицинских растений в Республике Молдова "AROMEDA", Институте химии, Институте Микробиологии и Биотехнологии, Кишинев, Молдова.

INGA ZINICOVSCAIA

IMPACTUL UNOR METALE DETERMINATE PRIN ANALIZA DE ACTIVARE CU NEUTRONI ASUPRA CALITATII MEDIULUI AMBIANT

145.01. CHIMIA ECOLOGICĂ

Rezumatul tezei de doctor habilitat în stiințe chimice

Aprobat spre tipar: 20.10.2022	Formatul hârtiei 60x84 1/16
Hârtie ofset. Tipar ofset.	Tiraj 25 ex.
Coli de tipar.: 1,6	Comanda nr. 225608

Tipografia Artpoligraf SRL
str. Henri Coanda 7, MD 2004
office@artpoligraf.md