

ECONOMICA



A SZOLNOKI FŐISKOLA TUDOMÁNYOS KÖZLEMÉNYEI
VIII. ÚJ ÉVFOLYAM 3. SZÁM, 2015.

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A tartalomból: Athina Zikouli: Environmental Protection and Rural Development in the Forests of the Democratic Republic of the Congo: How? ● Róbert Bagdi – Attila Szabó: Ecotourism in the Region of Lake Tisza ● Csizmadia Ivett Anita: Területfejlesztés: a geotermikus energia szerepe egy kisváros fejlődésében ● Fekete Péter Pál: Ki viszi a puskát? – avagy a vadkárak megítélésének egyes kérdései az új Ptk. tükrében ● Herman Petra - Harangi Sándor - Simon Edina - Baranyai Edina: Zooplankton szervezetek nehézfém terhelésének vizsgálata atomspektroszkópiai módszerekkel ● Kolcsár Helga: A Nyikó menti árvizek lehetséges okainak és következményeinek vizsgálata ● Krakker Anna: Környezeti nevelés élményalapú módszerekkel

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BEFEKTETÉS A JÖVŐBE

Tartalom

ELŐSZÓ	6
<i>Preface.....</i>	<i>6</i>
Athina Zikouli.....	7
Environmental Protection and Rural Development in the Forests of the Democratic Republic of the Congo: How?	7
<i>Környezetvédelem és vidékfejlesztés a Kongói Demokratikus Köztársaság erdeiben: de hogyan?</i>	<i>7</i>
Róbert Bagdi – Attila Szabó	10
Ecotourism in the Region of Lake Tisza.....	10
<i>Ökoturizmus a Tisza-tavi régióban</i>	<i>10</i>
Czékus Borisz - Udvardi Ildikó.....	22
Egyetemistáink szemete	22
<i>The Young of Subotica and their Refuse</i>	<i>22</i>
Márton Czikkely - Samuel Meier - Ágnes Bálint	28
The Study of Heavy Metal Adsorption on the Surface of Fungi Compost.....	28
<i>Nehézfém adszorpció vizsgálata gomba komposzt felületen</i>	<i>28</i>
Csákvári Edina.....	35
Egy Vág és Garam közti település (Marcelháza) gazdálkodásának átalakulása a XIX.-XX. században	35
<i>The Change of the Agriculture of a Settlement between the Rivers Váh and Hron in the 19-20. Centuries.....</i>	<i>35</i>
Csege Gyula - Gáll Tamás.....	45
Biztonságtudomány és a természetvédelem összefüggései	45
<i>The Interdependances of the Science of Safety and Environmentalism</i>	<i>45</i>
Csizmadia Ivett Anita	54
Területfejlesztés: a geotermikus energia szerepe egy kisváros fejlődésében	54
<i>Regional development: The Role of Geothermal Energy in the Development of a Small Town ...</i>	<i>54</i>
Csumán András - Gáti Péter - Sárközi Edit - Angyal Zsuzsanna - Bódi Barbara - Kasza Gyula - Kardos Levente	60
Kommunális szennyvíziszap 15 hetes laboratóriumi vermikomposztálásának tapasztalatai	60
<i>The Findings of 15-Week Laboratory Vermicomposting Experiments of Communal sewage Sludge</i>	<i>60</i>
Dávid Ildikó Nóra - Angyal Zsuzsanna - Kardos Levente	74
Városi közlekedésből származó légszennyezettség vizsgálata különböző növényrészek elemzése alapján	74
<i>The Examination of Air Pollution from Urban Transport Based on Testing Different Parts of Plants.....</i>	<i>74</i>

Fekete Péter Pál	85
Ki viszi a puskát? – avagy a vadkárok megítélésének egyes kérdései az új Ptk. tükrében	85
<i>Who Carries the Gun? – or Certain Questions in Connection with Game Damages in the Light of the New Civil Code</i>	85
Firgi Tibor	95
Települési hulladék domb alakváltozás vizsgálata	95
<i>The Examination of the Deformation of an MSW Hill</i>	95
Golovics József	105
Hatékony árvízvédelem: központosítás vagy decentralizáció?	105
<i>Efficient Flood Control: Centralization or Decentralization?</i>	105
Gönczi Gergely	115
A vietnámi háború folyamán elszenvedett kártételek ökológiai eredetű vonatkozásai	115
<i>An Ecological View on the Damage Caused throughout the Vietnam War</i>	115
Győri Barnabás	122
Napelemekkel előállított villamosenergia mennyiségének összehasonlító elemzése Magyarország és Németország vonatkozásában	122
<i>The Comparative Analysis of the Quantity of Electricity Produced by Solar Panels Regarding Germany and Hungary</i>	122
Herman Petra - Harangi Sándor - Simon Edina - Baranyai Edina	128
Zooplankton szervezetek nehézfém terhelésének vizsgálata atomspektroszkópiai módszerekkel	128
<i>The Investigation of Zooplankton Organisms Polluted with Heavy Metal with Atomic Spectroscopic Methods</i>	128
Kaczur-Somfay Dorottya	137
A magyarországi hulladékgazdálkodással kapcsolatos kommunikáció újragondolása	137
<i>A Possible Research Method For Exploring Hidden Relations in Ecological Communication</i>	137
Kaluzsa Anikó	148
A biogáz keletkezésének folyamata a szennyvíziszap rothasztása során.....	148
<i>The Process of the Formation of Biogas from Wastewater</i>	148
Kaszap Adrien	154
Réz és kadmium kezelés hatása talajok gombaközösségeire laboratóriumi kísérletben	154
<i>The Effect of Copper and Cadmium Treatment on the Soil Fungal Communities</i>	154
Kolcsár Helga	165
A Nyikó menti árvizek lehetséges okainak és következményeinek vizsgálata	165
<i>The Possible Causes and the Consequences of Flash-Floods in the Nyikó Basin</i>	165
Kovács Enikő	173
Energiatudatosság a magyar földrajztanításban – megújuló energiákra vonatkozó ismeretek nevelési-oktatási lehetőségei.....	173
<i>Energy-Awareness in the Hungarian Geography Teaching – The Educational Aspects of Renewable Energy</i>	173

Kovács Sárkány Hajnalka - Kovács Vilmos	179
Az élelmiszerek nyomon-követhetősége és a fogyasztókkal kapcsolatos aspektusai a vajdaságban	179
<i>The Product Traceability of Food Products and Consumer Awareness and Behaviour in Vojvodina</i>	179
Kovács Vilmos - Kovács Sárkány Hajnalka	186
Eredetvédelem és nyomon követhetőség a vajdasági agráriumban	186
<i>Protected Origin Status and Traceability in Agriculture in Vojvodina</i>	186
Kovács Vilmos - Kovács Sárkány Hajnalka - Lálity Zsolt	192
A földieper termesztése és nyomon követhetősége Vajdaságban	192
<i>Strawberry Production and Traceability in Vojvodina</i>	192
Kraker Anna	199
Környezeti nevelés élményalapú módszerekkel	199
<i>Training for Environmental Awareness and Sustainability</i>	199
Márton Ivett	207
Az egyedi tájértékek felvételezésén alapuló turisztikai célú fejlesztések bemutatása Egerszalókon	207
<i>Tourist Developments Based on the Survey of Unique Landscape Values in Egerszalók</i>	207
Máthé Ágnes Réka - Köhler Artúr	217
Kerozinnal szennyezett terület hidraulikai, vízminőségi és mikrobiológiai szempontú vizsgálata	217
<i>The Hydraulic, Water Quality and Microbiological Investigation of a Kerosene Contaminated Site</i>	217
Mayer Viktorné Noémi	226
Az alsó tagozatos környezeti nevelés hatása a gyermekek környezettudatos életmódjára	226
<i>The Impact of Environmental Education at Elementary School on Children's Environmentally Conscious Lifestyle</i>	226
Igor Molchanov	236
The State and Social Regulation of the Effectiveness of the Universities in Russia: a Systemic Approach and Monitoring	236
<i>Az oroszországi egyetemek állami és társadalmi szabályozása: szisztematikus megközelítés és monitoring</i>	236
Németh Anna	240
A mezőgazdaság relokalizációja a környezetterhelés csökkentése érdekében	240
<i>The Relocalization of Agriculture with a View to Reduce the Environmental Impacts</i>	240
Kehinde Olagunju - Ogunniyi Adebayo	252
The Assessment of the Impact of Rural Infrastructure on Rural Poverty in Nigeria	252
<i>A vidéki infrastruktúra vizsgálata Nigéria egy fejlődő régiójában</i>	252
Oláh Béla	258
A gépfenntartás jelenlegi helyzetének felmérése a mezőgazdaságban	258
<i>A Survey of the Current State of the Machine Maintenance in Agriculture</i>	258

Pecsenyánszky Melinda	266
Hiányszakmák, felnőttképzés, szakképzés heves megyében	266
<i>Shortage Occupations, Adult Education and Vocational Training in Heves County</i>	266
Páble Diána	278
Vadvirágos és gyógynövényes-vadvirágos magkeverékek vizsgálata	278
<i>The Investigation of Mixtures of Wildflower and Herb-Wildflower Seeds</i>	278
Gábor Dénes Szabó	285
Bioeconomy's Relevance in Hungary – the Assessment of a Survey	285
<i>A biogazdaság magyarországi vonatkozásai – egy kérdőív eredményeinek tükrében</i>	285
Szaniszló Albert – H.E.A.F. Bayoumi – Bálint Ágnes	294
Alternatív termőhely, mint új lehetőségek alkalmazása a biológiai szennyvíztisztításban	294
<i>Alternative Habitat as the Application of New Biological Wastewater Treatment Opportunities</i>	294
Szeberényi András	301
„Zöld energiával a zöld Magyarorszáért” honlap marketing szempontú elemzése saját kutatások alapján	301
<i>"Green Energy for Green Hungary" the Marketing Analysis of a Website on the Basis of Primary and Secondary Research</i>	301
Tar Ferenc	312
Közoktatási migráció és az iskolák társadalmi összetételének kapcsolata Szabolcs-Szatmár-Beregben.....	312
<i>The Relationship between the Migration in Primary Schools and the Social Composition of Schools in Szabolcs-Szatmár-Bereg County</i>	312
Tóth Csilla Noémi - Károlyi Anikó - Baranyai Edina - Fábíán István	324
Biológiai és környezeti minták vizsgálatát célzó analitikai módszerek kidolgozása mikrohullámú plazma atomemissziós spektrometriával	324
<i>The Elaboration of Analytical Methods for the Examination of Biological and Environmental Samples by MP-AES Method</i>	324
Udvardi Ildikó - Czékus Borisz	334
Mebénították a Bács-eret Topolyánál.....	334
<i>Water Pollution of Creek Krivaj at Backa Topola</i>	334
Usman Zainab A. - Oyetunde Muideen O.	341
The Role of Women in Agriculture, the Environment and Sustainable Rural Development: a Case Study of Nigeria	341
<i>A nők szerepe a mezőgazdaságban, a környezetvédelemben és a fenntartható vidékfejlesztésben: esettanulmány Nigériából</i>	341
Várady Gábor - Erőss Attila - Angyal Zsuzsanna - Somogyi Adrienn - Bódi Barbara - Kasza Gyula - Kardos Levente	347
Kommunális szennyvíziszap félüzemi szintű vermikomposztálásának tapasztalatai	347
<i>The Findings of the Pilot Scale Vermicomposting Experiments of Communal Sewage Sludge</i>	347

Varga Zsolt - Béres András - Holes Annamária - Aleksza László	354
Házi és üzemi komposztok csírázásgátló hatásának értékelése tenyészedenyes modellkísérletben	354
<i>The Assessment of the Germination Inhibitory Effect of Different Composts of Households and Composting Plants</i>	<i>354</i>
Vojtela Tibor - Bak János - Kelemen Zsolt – Kocsis László – Hudoba Zoltán - Fenyvesi László	360
Állati takarmányozásra alkalmatlan alapanyagok előkészítésnek lehetőségei biogáz előállításához	360
<i>The Pretreatment of Alternative Biomass Materials for Biogas Purposes</i>	<i>360</i>
Szerzőink.....	368

Márton Czikkely - Samuel Meier - Ágnes Bálint

The Study of Heavy Metal Adsorption on the Surface of Fungi Compost

Czikkely Márton - Meier Samuel - Bálint Ágnes

Nehézfém adszorpció vizsgálata gomba komposzt felületen

Összefoglaló

A nehézfém adszorpció gomba komposzt felületen az egyik alternatív technológia. Jelen tanulmányban gomba komposztokat használtunk és megmértük a nehézfém adszorpciós kapacitásukat. Laboratóriumi módszerekkel nehézfém oldatokat készítettünk, a nehézfémek adszorpcióját a gomba komposzt felületen rázással értük el, a minta degradálását és az analitikai méréseket ICP tömegspektrométerrel végeztük. A gomba komposzt nehézfém adszorpciós tulajdonságai felhasználhatók a szennyvízkezelésre, mert a szennyvíz néha nagy koncentrációban tartalmaz nehézfémeket.

Kulcsszavak: nehézfém, komposzt, adszorpció, felület

Abstract

The heavy metal adsorption on the surface of fungi compost is one of the alternative technologies. In this study fungi composts were used and we measured the heavy metal adsorption capacities. The laboratorial methods were the preparing solutions of heavy metals, the adsorptions of heavy metals on the surface of fungi compost by shaking method, the sample degradation and the analytical measurements by ICP-MS. The heavy metal adsorption properties of fungi compost could be used in wastewater treatment because wastewater sometimes contains a high concentration of heavy metals.

Keywords: heavy metal, compost, adsorption, surface

Introduction

The renewable and alternative energy sources are perfect environmental safety technologies. The wastewater treatment is one of the most used environmental technologies. The degradation of heavy metal contents of communal and industrial wastewaters is a key question. Many organic and inorganic materials have been used for heavy metal removal in the last years, such as grape stalk waste, sewage sludge, algae, peat, wool fibres, algal biomass, cotton boll, tree bark, sugar beet pulp, activated carbon fibres and other agricultural products (Kang et al., 2008; Zhang, 2011).

The heavy metal adsorption on surface of fungi compost is one of the alternative technologies. In this study were used fungi composts and we measured the heavy metal adsorption capacities. The laboratorial methods were the preparing solutions of heavy metals, the adsorptions of heavy metals on the surface of fungi compost by shaking method, the sample degradation and the analytical measurements by ICP-MS.

The heavy metal adsorption properties of fungi compost could be used in wastewater treatment because wastewaters sometimes contain high concentrations of heavy metals.

Other heavy metal adsorption studies

Wastewater containing copper and cadmium can be produced by several industries. The increasing awareness of accumulation of heavy metals in the environment has led to new and improved cleaning technologies. In this regard, an innovative heavy metal removal process composed of biosorption and sedimentation was developed (Bakkaloglu et al., 1998).

The study of Bakkaloglu et al. (1998) covers the comparison of various types of waste biomass including bacteria, yeast fungi and activated sludge for their efficacy in the biosorption, sedimentation and desorption stages in the removal of zinc, copper and nickel ions. In the biosorption studies carried out with single metal solutions, *A. nodosum*, *S. simosus* and *F. vesiculosus* proved to be the best biosorbents for zinc, copper and nickel ions respectively. Overall, among the biomass tested, *A. nodosum*, *S. simosus*, *F. vesiculosus* and *P. chrysogenum* were found to have the highest potential for use in the heavy metal removal process.

The occurrence and the fate of heavy metals (Cd, Pb, Mn, Cu, Zn, Ni and Fe) during the wastewater treatment process were investigated by Karvelas et al. (2003) in the wastewater treatment plant of the city of Thessaloniki (Greece), operating in the activated sludge mode. The wastewater and sludge samples were collected from six different points of the plant, namely: the influent and the effluent of the primary sedimentation tank, the effluent of the secondary sedimentation tank, sludge from the primary sedimentation tank, activated sludge from the recirculation stream. An exponential correlation was found between the metal partition coefficient, $\log K_p$, and the suspended solids concentration. The mass balance of heavy metals in the primary, secondary and the whole treatment process showed good closures for metal species (Karvelas et al., 2003).

All heavy metals were detectable in the wastewater samples with a frequency of

occurrence about 100% and only Pb was detected at lower frequency (90%). Karvelas et al. (2003) reported that the phase distribution of individual metals exhibited only little change during the treatment process with a slight progressive increase of the dissolved phase of some metals after each treatment step. Ulmanu et al. (2003) reported in their study that the sorption of copper and cadmium ions using activated carbon, waste materials (such as compost, cellulose pulp waste and anaerobic sludge) as sorbent. The study shows that copper being preferentially adsorbed by all materials with the exception of anaerobic sludge (Quan Y.C. et al., 2007).

Qudais and Moussa (2004) presented that reverse osmosis (RO) and nanofiltration (NF) technologies for the treatment of wastewater containing copper and cadmium ions to reduce environmental degradation was investigated. The synthetic wastewater samples containing copper and cadmium ions at various concentrations were prepared in the laboratory. The results showed that high removal efficiency of the heavy metals remove could be achieved by Ro process (98% and 99% for copper and cadmium). Copper ions were successfully removed from the wastewater by Ro and NF.

The concentration of copper in the product water (permeate) for RO was reduced to an average value $3,5 \pm 1,7$ ppm with an average removal efficiency of 97% (Qudais and Moussa, 2004).

Seelsaen et al. (2005) reported the sorption experiments were used to access the ability of various materials (compost, sand) to remove heavy metal contaminants typically found in storm water. The compost had the best physicochemical properties for sorption of heavy metal ions (Cu and Cd). The compost sorption properties conformed by the linear form (Langmuir equation) for Zn (II) being 11,2 mg/g at pH 5. Various combinations of compost, sand and other materials were observed to have excellent heavy metal removal properties (Zn: 75-96%, Cu: 90-93%).

Selling et al. (2008) have shown that the heavy metal sorption data were used to determine the sorption efficiency of Cu (92%), Zn (88%) and Pb (97%) by mix of sand and compost. The relative sorption affinity of these metals by compost plus sand is in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$. The heavy metal sorption conformed to the linear form of Freundlich isotherm (Seelsaen et al., 2007).

Compost with a smaller particle size fraction has larger surface areas and greater sorption properties than the larger particle size fraction. The aim of Kocasoý and Grvener (2008) research was to determine the retention capacity of compost for Cu, Zn, Ni and Cr.

Composting is a stabilization process of aerobic decomposition. It leads to the development of microbial populations which causes numerous physico-chemical changes in the mixture. Composting can reduce the mixture volume by ~50%. Destroy the pathogens by the metabolic heat generated by the thermophile phase, degrade a big number of hazardous organic pollutants (Qudais and Moussa, 2004).

Materials and methods

Fungi compost samples

Fungi compost samples were used for these measurements. Fungi compost is a special compost type; it contains some important chemical and biochemical matters for fungi. The properties of fungi compost samples:

pH: 6,9
dry matter content: 35%
N content: 0,8%
P content: 0,6%
K content: 0,9%
Ca content: 3,0%
Mg content: 0,3%

The fungi compost samples came from a small composting company (porka, Hungary). The sampling period was between 04/06/2014 and 16/08/2014.

Preparing and shaking samples

The single, double and triple combinations of heavy metals were used for preparing solutions and analytical measurements. The list of single, double and triple heavy metal elements of prepared solutions (Table 1).

Table 1. The combinations of heavy metals

Single elements	Double elements	Triple elements
Mn	Mn+Cu	Cd+Zn+Mn
Cd	Zn+Cd	Cu+Mn+Zn

All the solutions of every single, double and triple element were prepared in each concentration (in three repeats): 250 mg/dm³; 500 mg/dm³; 750 mg/dm³ and 1000 mg/dm³ (Figure 1). All solutions were prepared with de-ionized water (18 MΩcm⁻¹) from a Milli-Q analytical water preparing system.

Figure 1. Preparing the sample solutions



(Photo: Márton Czikkely)

The adsorptions of heavy metals on the surface of fungi compost were researched by shaking method. 10 g of fungi compost sample and 30 cm³ solution of heavy metals were taken into centrifugal tubes to the better adsorption. (Figure 2). The shaking time was 50 min and the rotation was 480/min.

Figure 2. The shaking method and the centrifugal tubes



(Photo: Márton Czikkely)

Degrading of samples

All of the samples were degraded because the organic matter content could disturb the correct measure of heavy metal content. Milestone 1200 Microwave degrading machine was used to sample degrading. 5 cm³ HNO₃ and 1 cm³ H₂O₂ acid reagents were added to 5 cm³ shaken sample. The degrading time was 24 min. After the degrading the water bath time was 30 min. The final step of the whole degrading programme was the degraded sample diluting to 25 cm³.

The setup and steps of the degrading programme:

1 st step:	6 min and 250 W
2 nd step:	6 min and 400 W
3 rd step:	6 min and 650 W
4 th step:	6 min and 250 W

Measure with ICP-MS

Measure with Inductively Coupled Plasma with Mass Spectrometry (ICP-MS) is a powerful analytical method for the determination of metals e.g. Cd, Cu, Ni, Zn, and Mn (Selling et al., 2008).

The ICP-MS analytical method is sensitive and allows for the simultaneous analysis of elements and their isotopes (Beck et al., 2002).

We used an ICP-MS (Agilent 7500ce - Agilent Technologies, Waldbronn, Germany - equipped

with autosampler) at the Institute of Analytical Chemistry, University of Vienna, Austria (Figure 3).

Figure 3. The ICP-MS combined with the autosampler



(Photo: Márton Czikkely)

All of the instrumentations and parameters of the used ICP-MS listed in Table 2.

Table 2. Specifications of the used ICP-MS

Specifications	Parameters of the ICP-MS
ICP Frequency	27,12 MHz
Detection limit	Low (in ppt range)
Mass filter	Hyperbolic Quadrupole
Mass frequency	~ 3 MHz
Detector	Electron multiplier
Vacuum system	3 stage vacuum system
Pump	Rotary pump Turbo molecular pump
Autosampler type	Cetax ASX-520 (Nebraska USA)
Maximum number of samples at one time (in the autosampler)	360 samples

(ICP-MS 7500ce manual – see [http1 reference](#))

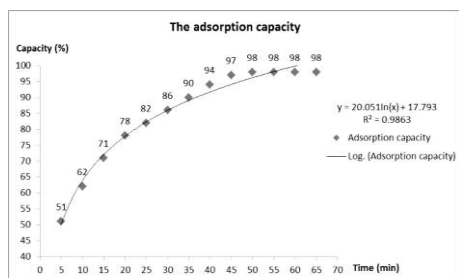
Results and discussions

In this study the best shaking time and the ICP-MS measures were determined to research the capacity and method of adsorptions of heavy metals on surface of fungi compost.

Choose the best time to adsorbing

The adsorption capacity was measured several times: in 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 and 65 min. The following diagram (Figure 3) shows the changes of adsorption capacity [%] in times [min]. The measures show the best adsorption capacity in 50 min (the capacity was 98%). The measuring in 50, 55, 60 and 65 min shows the same result.

Figure 4. The changes of adsorption capacity



All the samples were shaken for 50 min because of the best heavy metal adsorption.

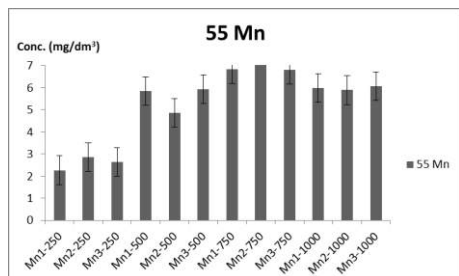
Isotope interferences

The isotope interferences are important to determine the percentages of heavy metal isotopes in samples. The following table shows the potential interferences for isotopes (Table 3).

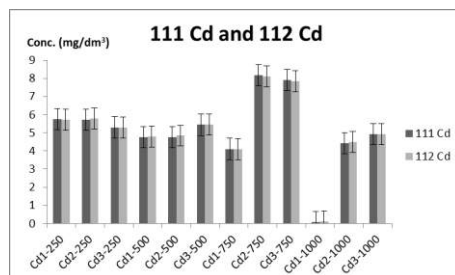
Adsorbing from single elements

The solutions contain single elements were the first adsorbing test before the combinations.

The 55 Mn adsorbing was better in the higher concentrations but 500; 750 and 1000 mg/dm³ produced the same result. The adsorbing capacity in highest concentrations could not be the limit.



The 111 Cd and 112 Cd produced the same result and the adsorption could not depend on the isotope numbers.



Double elements adsorptions

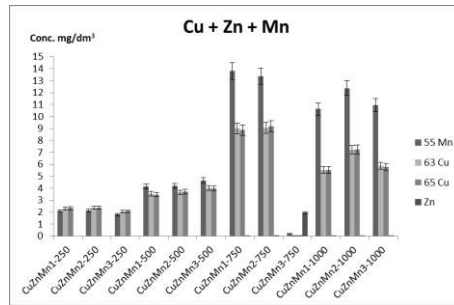
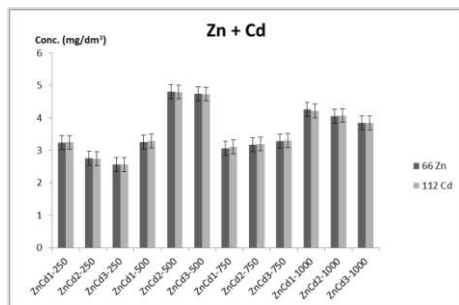
Double elements contains solutions were the following: Zn+Cd and Mn+Cu.

The Zn+Cd combination produced unique results because the 500 mg/dm³ concentration produced the highest adsorbing capacity.

Table 3. Potential interferences

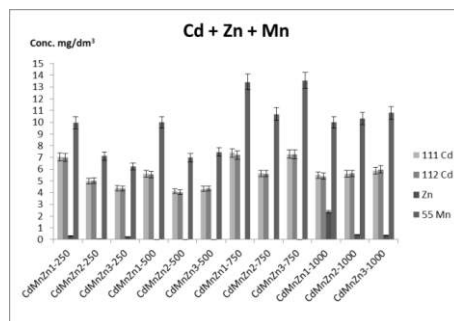
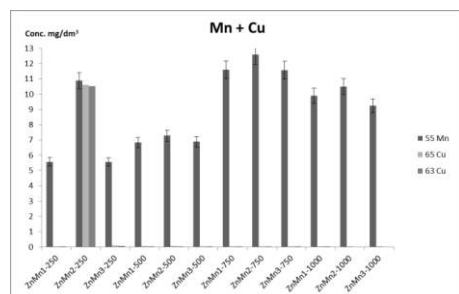
Mass	Elements	Isotopic abund. (%)	Potential polyatomic interfer.	Interference isotopic abund. (%)
55	⁵⁵ Mn	100	³⁹ K ¹⁶ O ¹⁵ N ⁴⁰ Ar	93 0,4
56	⁵⁶ Fe	91,7	³⁹ Ar ¹⁶ OH ⁴⁰ Ar ¹⁶ O	0,06 99
57	⁵⁷ Fe	2,2	⁴⁰ Ca ¹⁶ O ⁴⁰ Ar ¹⁷ O	97 0,04
58	⁵⁸ Fe ⁵⁸ Ni	0,28 68,3	⁴⁰ Ar ¹⁶ OH ⁴¹ K ¹⁶ O ⁴⁰ Ar ¹⁸ O	99 7 0,2
59	⁵⁹ Co	100	⁴⁰ Ar ¹⁷ OH ⁴² Ca ¹⁶ O ⁴⁰ Ca ¹⁸ O	0,04 0,6 0,2
63	⁶³ Cu	69,2	⁴⁰ Ar ¹⁸ OH ⁴³ Ca ¹⁶ O	0,2 0,1
64	⁶⁴ Zn	48,6	²³ Na ³⁶ Ar ²³ Na ⁴⁰ Ar	0,3 99,9
65	⁶⁵ Cu	30,8	²⁴ Mg ⁴⁰ Ar	79
66	⁶⁶ Zn	27,9	²⁵ Mg ⁴⁰ Ar ²⁶ Mg ⁴⁰ Ar	10 11
111	¹¹¹ Cd	12,8	⁹⁵ Mo ¹⁶ O	16
114	¹¹⁴ Cd	28,7	⁹⁸ Mo ¹⁶ O	24

(Beck et al., 2002, p. 17. and printed Measuring Manual for ICP-MS in the Institute of Analytical Chemistry at the University of Vienna)



The adsorption of Mn + Cu was different than the Zn + Cu. The concentration of 250 mg/dm³ shows the three (55 Mn + 63 Cu + 65 Cu) elements adsorption. The other results show only the Mn adsorption.

The Cd + Mn + Zn triple combination also shows the highest adsorption capacity of Mn. The 55 Mn had a better adsorption capacity than the other elements because of the better chemical and physical properties.



Triple elements

The adsorption of Cu + Zn + Mn shows the highest capacity of Mn adsorption and the lowest adsorption of Zn.

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