ECONOMICA VIII. ÚJ ÉVFOLYAM 3. SZÁM, 2015.

# ECONOMICA

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

ECONOMICA

A Szolnoki Főiskola Tudományos Közleményei
VIII. új évfolyam 3. szám 2015.



Felelős kiadó:
Dr. Túróczi Imre PhD, főiskolai tanár
a Szolnoki Főiskola rektora



Szerkesztőség címe:
Szolnoki Főiskola, 5000 Szolnok, Tiszaligeti sétány 14.

A folyóirat korábbi számai letölthetők:
http://tudomany.szolfportal.hu/economica

A folyóirat borítója és grafikai arculata Bodolai Mária munkája
Nyomdai munkálatok:
Alumni Kiadó Kft.
Bereczki Csaba ügyvezető

ISSN 1585-6216

Projekt azonosító:
TÁMOP-4.2.2.B-15/1/KONV-2015-0015
"Tehetséggondozási kutatóműhelyek fejlesztése
a Szolnoki Főiskolán"

SZÉCHENYI 2020

MAGYARORSZÁG KORMÁNYA

Európai Unió
Európai Szociális
Alap

BEFEKTETÉS A JÖVŐBE

# Tartalom

**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 gompa 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 laboratorical 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 laboratorical 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 craned 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 form the recirculation stream. An exponential correlation was found between the metal partition coefficient, logKp, 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 ± 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 Kocasoy and Grüvener (2008) research was to determine the rention 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 (Áporka, Hungary). The sampling period was between 04/06/2014 and 16/08/2014.

*Preparing and shaking samples*

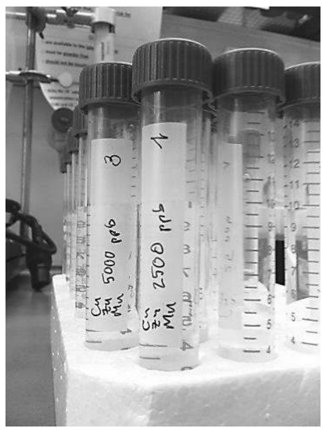
The single, double and triple combinations of heavy metals were used for preparing solutions and analytical measurements. The list of single, double and triple heavy metal elements of prepared solutions (Table 1).

**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/dm$^3$; 500 mg/dm$^3$; 750 mg/dm$^3$ and 1000 mg/dm$^3$ (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 cm$^3$ 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 $cm^3$ $HNO_3$ and 1 $cm^3$ $H_2O_2$ acid reagents were added to 5 $cm^3$ 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 $cm^3$.

The setup and steps of the degrading programme:

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

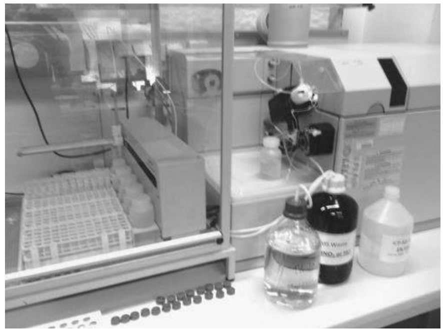
*Measure with ICP-MS*

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<br>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)*

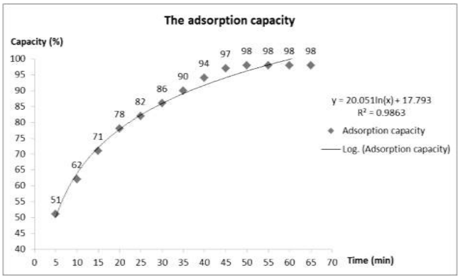
## Results and discussions

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.

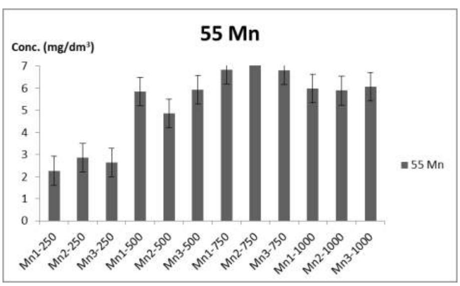
*Isotope interferences*

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).

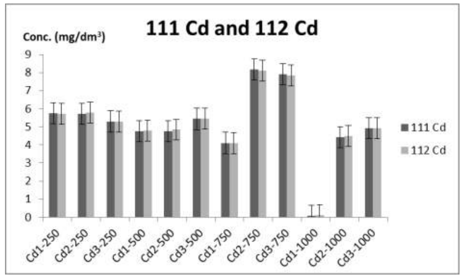
*Adsorbing from single elements*

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/dm$^3$ 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*

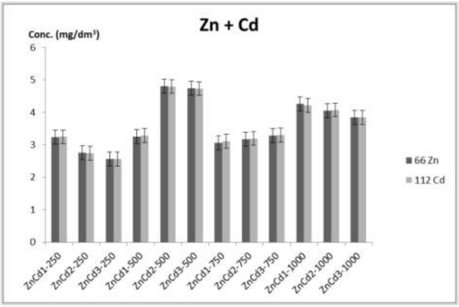
Double elements contains solutions were the following: Zn+Cd and Mn+Cu.

The Zn+Cd combination produced unique results because the 500 mg/dm$^3$ concentration produced the highest adsorbing capacity.

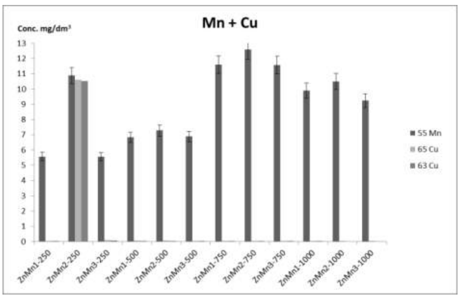
**Table 3. Potential interferences**

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

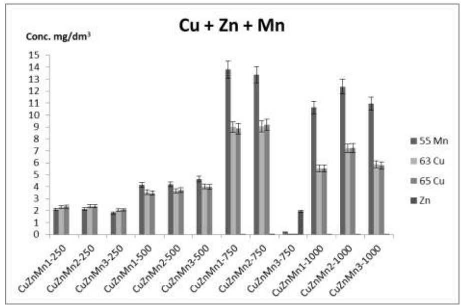



The adsorption of Mn + Cu was different than the Zn + Cu. The concentration of 250 mg/dm$^3$ shows the three (55 Mn + 63 Cu + 65 Cu) elements adsorption. The other results show only the Mn adsorption.

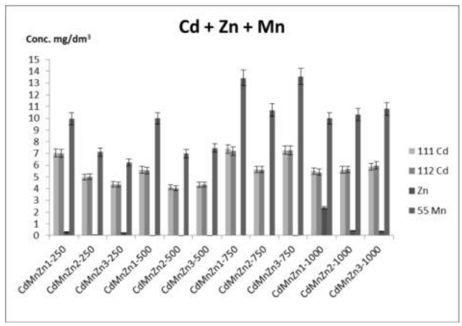



*Triple elements*

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




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.




## References


[1.] K.C. Kang, S.S. Kim, J.W. Choi, S.H. Kwon 2008: Sorption of Cu2+ and Cd2+ onto acid and base-pre-treated granular activated carbon and activated carbon fibre samples, J. Ind. Eng. Chem. 14. p. 131–135.

[2.] N. Seelsaen et al. 2005: Pollutant removal efficiency of alternative filtration media in storm water treatment. Water Science and Technology 54 (6-7): 299-305.

[3.] R. Selling et al. 2008: Two-stage anaerobic digestion enables heavy metal removal. Water Science and Technology 57 (4): 553-558.

[4.] N.G. Beck, R.P. Franks, K.W. Bruland 2002: Analysis for Cd, Cu, Ni, Zn, and Mn in estuarine water by inductively coupled plasma mass spectrometry coupled with an automated flow injection system. Analytica Chimica Acta 455: 11–22.

[5.] Http1:http://www.concordia.ca/content/dam/artsci/research/cbams/docs/7500ceICP-MShardwaremanualen.pdf ICP-MS Agilent 7500ce Hardware Manual (pdf file). Agilent official product. Downloaded: 03/07/2014

[6.] Measuring Manual to ICP-MS for MSc students (2014). Ed.: Prof. Dr. Christopher Gerner and Michael Größl. Institute of Analytical Chemistry, University of Vienna.

[7.] "Analysis of High Matrix Environmental Samples with the Agilent 7500ce ICP-MS with Enhanced ORS Technology" Agilent Technologies publication 5989-0915EN www.agilent.com/chem

[8.] Quan-Ying Cai, Ce-Hui Mob, Qi-Tang Wu, Qiao-Yun Zeng, Athanasios Katsoyiannis 2007: Concentration and speciation of heavy metals in six different sewage sludge-composts. Journal of Hazardous Materials 147: 1063–1072.

**Acknowledgements**

This work was financed by the Balassi Institute (Hungary) and the Institute of Analytical Chemistry (in University of Vienna, Austria). The authors would like to thank following people for their help and cooperation:

Dr. Csaba Dobolyi (Szent István University, Hungary)
Prof. Dr. Christopher Gerner, Sarah Teiner and Matthias Klose (University of Vienna, Austria)