Heavy metal treatment by a new adsorption method from polluted drinking waters

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Abstract: *Removal of heavy metal contents from communal and industrial wastewaters is a key question. The high concentration of heavy metals (up to the pollution level/concentration) could disturb the normal ecosystems of rivers. The heavy metal treatment must be used to save the ecosystem and clean drinking waters. Many organic and inorganic materials have been used to heavy metal elimination in the last years, such as grape stalk waste, sewage sludge, algae, peat, wool fibres, algal biomass, cotton ball, tree bark, sugar beet pulp, activated carbon fibres and other agricultural products. Our new scientific result is the adsorption on a surface of a special fungi compost and the determination of the adsorption capacity. In this study, fungi composts were used and the heavy metal adsorption capacity was measured. The laboratory 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 results show the successfully new adsorption method. The heavy metal adsorption properties of fungi compost could be used in wastewater treatment because wastewaters sometimes contain high concentrations of heavy metals.*

Key Words: *drinking water, heavy metals, adsorption, method development.*

1. INTRODUCTION:

Wastewater containing copper and cadmium can be produced by different types of industries. The average increasing of heavy metal accumulation in the environment has led to new and improved cleaning technologies. In this regard, an innovative heavy metal removal process composed of biosorption was developed [1].

The study of [2] shows the result of heavy metal measurements with ICP-MS. Their conclusions were applied in our study also. They determined the full method of measurements from the injection to the data analyse. The ICP-MS technique is sutibale for the measurement of different heavy metal concentrations in natural water samples [2].
[3] studied heavy metals' and PAH's concentrations in agricultural and urban water samples. They determined the relationship between the heavy metal concentrations and the agricultural produces.

The study of [4] covers the comparison of various types of waste biomass including bacteria, yeast fungi and activated sludge for their efficiency in the biosorption, sedimentation and desorption stages in the removal of zinc, copper and nickel ions. Single heavy metal solutions were studied in the biosorption experiments. In point of wiev of biosorption (in case of zinc, copper and nickel) was found the best the next bacterias A. nodosum, S. simosus and F. vesiculosus. 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 [4] [5].

The occurrence and the fate of heavy metals (Cd, Pb, Mn, Cu, Zn, Ni and Fe) during the wastewater treatment process were investigated in wastewater settlement of the city of Thessaloniki (Greece), operating in the activated sludge mode [6]. The wastewater and sludge samples were collected from six different points of the settlement, 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 [7] [8].

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%). [9] reported that the phase distribution of individual metals exhibited only small change during the treatment process with a slight progressive increase of the dissolved phase of some metals after each treatment step. [10] 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. According to the study the copper being preferentially adsorbed by all materials the exception of anaerobic sludge [11] [12].
[13] presented that reverse osmosis (RO) and nanofiltration (NF) technologies for the treatment of wastewater containing copper and cadmium ions to reduce environmental load. 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 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% [13][14][15] reported the sorption experiments were used to access the ability of various materials (compost, sand) to remove heavy metal contaminants typically found in stormwater. 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%).

[16] 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: Pb2+ > Cu2+ > Zn2+. The heavy metal sorption conformed to the linear form of the Freundlich isotherm [16] [17].

Compost with a smaller particle size fraction has larger surface areas and greater sorption properties than the larger particle size fraction. [17] aim of their research was to determine the sorption 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 to about 50%. Destroy the pathogens by the metabolic heat generated in the thermophile phase, degrade a big number of hazardous organic pollutants [14].

The study of [18] reported the results of heavy metal measurements in water samples. They measured the heavy metal (Cd, Cu, Hg, Pb) concentrations in water samples from Thoothukudi and Vizhinjam (in India). They also researched the possibility of heavy metal bioaccumulations with Phallusia nigra. The determined order of bioaccumulations: Hg – Cu – Cd – Pb.

Our research determined a new heavy metal adsorption method which could increase the adsorption efficiency by shaking. A special fungi compost was used as adsorbent and we researched the heavy metal adsorption properties of this special compost. Heavy metal soultions were used to determined the adsorption processes. The heavy metal solutions were prepared from Cu, Cd and Mn in single, double and triple combinations and in several concentrations [17] [18].

2. MATERIALS AND METHODS:

Fungi compost samples were used to realize all these measurements. The fungi compost samples derived from a small composting company (Áporka, Hungary). Fungi compost is a special compost type; it contains some important chemical and biochemical matters. The content of fungi compost samples were the following:

- pH: 6.9
- Dry matter content: 35.0%
- N content: 0.8%
- P content: 0.6%
- K content: 0.9%
- Ca content: 3.0%
- Mg content: 0.3%

The list of single, double and triple heavy metal elements of prepared solutions are presented in *Table 1*.

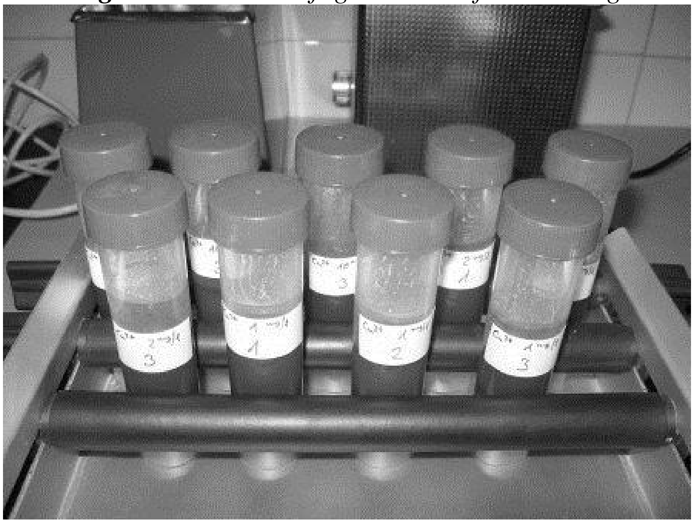
Table 1. *The prepared combinations of heavy metals*

Single elements	Double combinations
Mn	Mn, Cu
Cd	Mn, Cd

All of the solutions of every single, double and triple element combinations were prepared in each concentration (in three replicates): 250 mg/dm^3; 500 mg/dm^3; 750 mg/dm^3 and 1000 mg/dm^3. All solutions were prepared with MLQ water (18 MΩcm-1) from a Milli-Q analytical water preparing system.

The adsorptions of heavy metals on the surface of fungi compost were investigated by shaking. 10 g of fungi compost sample and 30 cm^3 solution of heavy metals were taken into centrifugal tubes to the better adsorption *(Figure 1)*. The shaking time was 50 min and the rotation velocity was 480/min. The shaking method has been developed at the Szent István University, Department of Chemistry and Biochemistry, Gödöllő, Hungary. All of the machine settings were used to measurements of all samples.

***Figure 1**. The centrifugal tubes before shaking*



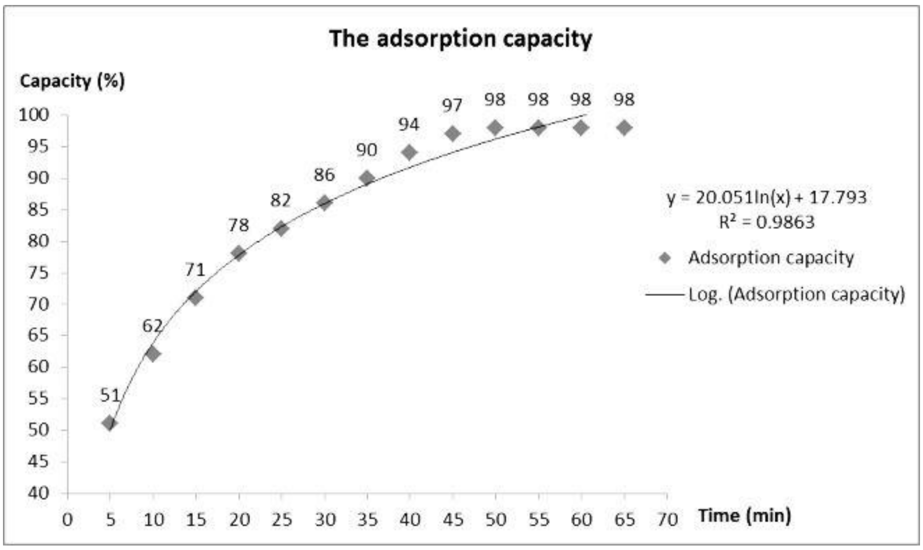
All of the samples were digested because the organic matter content could disturb the correct measurement of heavy metal content. Milestone Mega 1200 Microwave digestion machine was used to digest the samples. 5 cm^3 HNO_3 and 1 cm^3 H_2O_2 acid reagents were added to 5 cm^3 shaken sample. The digestion time was 24 min. After digesting the water bath time was 30 min. The final step of the whole digestion program the digested sample was diluted to 25 cm^3 (Sastre et al., 2012).

The measurement with Inductively Coupled Plasma coupled Mass Spectrometry (ICP-MS) is a powerful analytical method to determine of trace elements e.g. Cd, Cu, Ni, Zn, and Mn. The ICP-MS analytical method is sensitive and allows the simultaneous analysis of elements and their isotopes (Gerner and Größl, 2014). The isotope interferences are important to determine the percentages of heavy metal isotopes in samples. All of the instrumentations and parameters of the used ICP-MS are presented by Beck et al. (2002); p. 17. The ICP-MS (Agilent 7500ce - Agilent Technologies, Waldbronn, Germany - equipped with autosampler) was used at Institute of Analytical Chemistry, University of Vienna, Austria. The autosampler allows the simultaneous measurements of 150 samples.

3. RESULTS AND DISCUSSION:

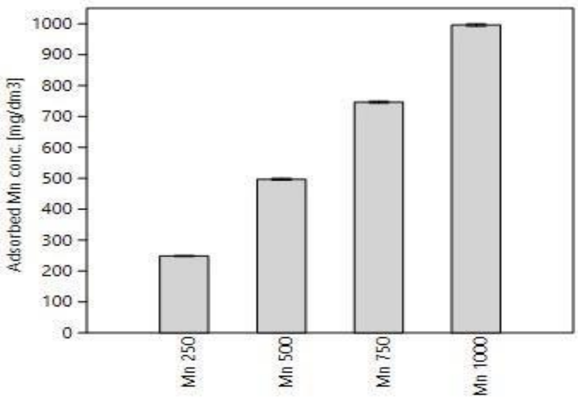
The adsorption capacity was measured in 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 and 65 min respectively. Figure 2 shows the changes of adsorption capacity [%] in function of times [min]. The adsorption capacities [%] were measured in 250 mg/dm^3 heavy metal concentration in every time. The results show the highest adsorption capacity for 50 minutes of shaking (the capacity was 98%). The measuring in 50, 55, 60 and 65 min presented the same result. According to our results all of the samples were shaken in 50 min in other experiments.

***Figure 2.** The changes of adsorption capacity at different shaking time*



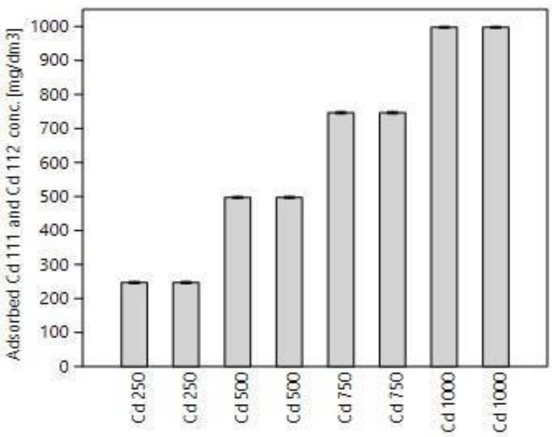
The solutions contain single elements were the first adsorbing test before the combinations. The adsorption of 55Mn (Figure 3) was best in the highest concentrations the adsorbing capacity in 750 mg/dm^3 and 1000 mg/dm^3 concentrations not the limit of adsorption capacity.

Figure 3. *Adsorption of 55Mn*



The Figure 4 shows the changes of Cd adsorptions in each concentrations. The adsorption of 111Cd and 112Cd (Figure 4) produced the same result and it may be concluded, that the adsorption could not depend on the isotope numbers. At 1000 mg/dm^3 the adsorpted concentration was the lowest. The reason of this value is the ion size of 111Cd and 112Cd because the biggest ions could not adsorbe perfectly in highest concentrations and the adsorption capacity depends on the ion size. This is the reason of the doubled and tripled heavy metal adsorptions also.

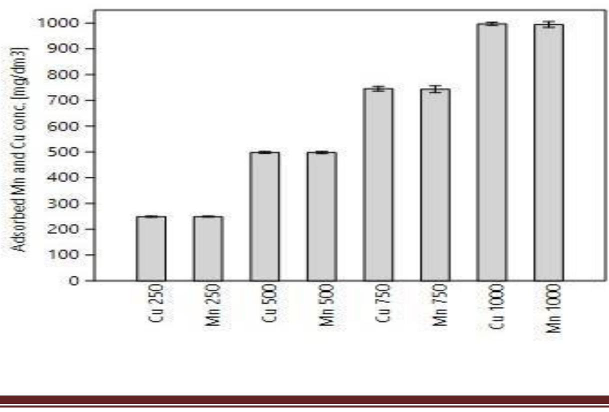
Figure 4. *Adsorptions of 111Cd and 112Cd*



Other solutions were prepared with double elements also. The results show the different adsorption capacity which is depends on the doubled element sizes. Some of these elements could stop the adsorption of others because the sizes are also different. The adsorption of biggest size element could result the bad adsorption of smaller size elements. The comparison of adsorption properties from doubled solutions and adsorption from single solutions could result the different adsorption in the same original concentration (e.g. the adsorptions of 55Mn was better in single content, and shows increase continously.

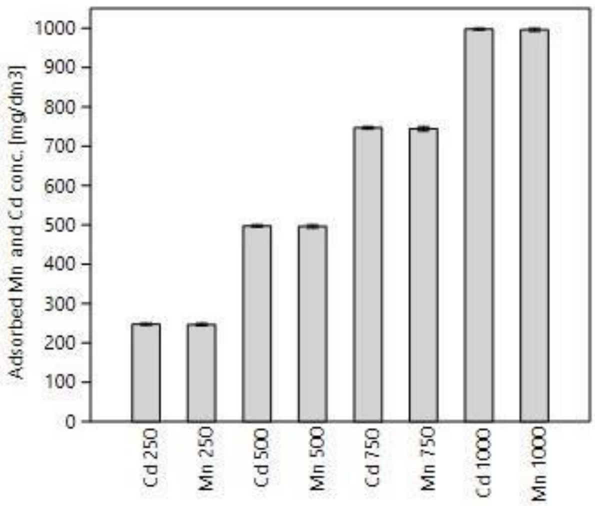
Solutions containing double elements contains were the following: 55Mn, 63Cu, 65Cu (Figure 5) and 55Mn, 111Cd, 112Cd (Figure 6). These two combinations produced unique results because the 500 mg/dm^3 concentrations produced the highest adsorbing capacity. After this concentration the adsorption capacity of the fungi compost was lower.

Figure 5. *Adsorptions of 55Mn, 63Cu and 65Cu*



The adsorption of 55Mn, 63Cu, 65Cu was different than the 55Mn, 111Cd, 112Cd. The concentration of 250 mg/dm^3 shows the three (55Mn + 63Cu + 65Cu) element adsorption. The other results show the 55Mn adsorption, only.

Figure 6. *Concentration of 55Mn, 111Cd and 112Cd in case of their combination in filtrate*



The high concentrations of heavy metals are important problems of cleaning waters (e.g. wastewater treatment, drinking water treatment). The heavy metal adsorption on surface of fungi compost is one of the alternative technologies of removing the heavy metal pollution from waters and wastewaters. The developing of new shaking method is the new scientific result to reach the best heavy metal adsorption.

In this research special fungi composts and different heavy metals in different combinations were used. The laboratory methods were used for 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.

4. CONCLUSION:

We have measured the adsorption properties of heavy metals in each concentration but we have to determine the best adsorption capacity with the determination the adsorption at highest concentrations. Should increase the concentration up to 1000 mg/dm3 and must combine heavy metals in other combination (triple combinations also). We have to develop the sahking method continously to fit with triple heavy metal combinations. We could determine the behaviour of all heavy metals if they are in the solutions in time. That will complement the whole heavy metal adsorption in polluted solutions.

After the laboratory practice must study the adsorption on wastewater treatment settlement. We have to decide the best place of this technology in order of wastewater treatment chain.

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