# EVALUATION OF POSSIBILITY OF PHYTOSTABILIZATION OF HEAVY METALS BY PLANTS

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***Abstract:*** *The purpose of this study was to investigate the effect of the spontaneously formated vegetation on the heavy metal concentration of a leather factory sewage sludge. The site of our investigatin consists of three staightly-connected sludge settling pounds. The main pollutant substance of the sludge is the chromium originated from the leather manufacturing process. The average total chromium concentration of the sludge was 30.000 ppm at the begining of our investigation. But the amount of the extremly toxicant chromium (VI) form was only 150 ppm, fortunately. In 1998, when the activity of the factory ended the three pounds has been overgrowen spontaneously by various plants. In 2001 we managed to identified 42 different plant specieses. The three most dominant specieses were the reed (Phragmites australis), the bulrush (Typha angustifolia) and the orach (Atriplex hastrata).*
***Keywords:*** *heavy metals, chromium, tannery waste, natural vegetation*

## 1. INTRODUCTION

The decline of leather industry in Central Europe in the late 1970's left behind hundreds of hectares of land contaminated with chromium as the major inorganic contaminant. Chromium was the main tanning agent in the manufacturing process of leather products. 30-40 litre 2 w/w % Cr (III) solution is needed to prepare one kilogram raw leather and the 40 % of chromium content leave in the solution and added to the effluent stream. The chromium contaminated sludge was deposited in sedimentation pond systems generally. Because of potential health risks these areas needed to high attention. For economic and also technical reasons, a remediation of these sites by physical or chemical procedures is not possible. The results suggest that remediation concepts should include natural processes.

Phytoremediation, that is recovering the health of soils or sediments contaminated with heavy metals by using green vegetation has today been a stimulating challenge for environmental protection all over the world (Salt et al. 1995). Among the phytoremediation processes, it is the in-situ inactivation technique that has special significance, since it reduces the dangers caused by the potential toxic impacts of heavy metals (Chaney 1983, Baker and Brooks

1989). Green covers are a true alternative solution, the intensive form of which being the use of crops while the extensive one in former wastewater settling pond systems the utilization of the natural vegetation.

Our study presents the results of the floristically and vegetation examinations performed in the units of a former secondary chromium contaminated sedimentation pond system of a Hungarian leather factory in . The outcome of analyses on the chromium content of the plants and the sediment samples will also be discussed. Moreover, the ration of Cr (III) and Cr (VI) in the samples was determined.

## 2. MATERIALS AND METHODS

The site of our investigation consists of three straight-line-connected sludge settling pounds. The area of the investigated ponds is 1000 square meter. In accordance with the vegetation period sampling was performed on four occasions. From the spring sampling on, floristical measurements were made in order to identify the plant species existing in the pond units. From the sampling sites plant and sediment from beneath the plant were collected for chemical analyses. The sampling depth was 1 metre in the sediment. Sediment and plant samples were dried in a drying-oven at 105 °C. Determination of heavy metal concentration after $HNO_3/H_2O_2$ extraction was performed with an ICP-AES method (SPEKTRO-SPEKTROFLAME ICP-AES). The control area was in the Botanical Garden of the University of Debrecen.

**Specification of the Cr VI (Posta and Gáspár 1996):**

Off line method

Separation: C18 reverse phase colonna

Method: flow injection analysis FIA

Concentrating agent: tetrabutil-ammonium-salt (TBA)

Detection: ICP-AES

## 3. RESULTS AND DISCUSSION

According to the observations, the units of the pond system can be floristically characterized by a relative diversity of species (56 species). The common reed (*Phragmites australis*), sea club-rush (*Bolboschoenus maritimus*), orach (*Atriplex ssp*.) and aster (*Aster punctatus*) can be considered as being existent in large masses, and the other weed also need to be mentioned. The green part covering varies from unit to unit, ranges between 85 and 100%, however,

regarding the previous years there occurs an advantages tendency of increasing green covering.

Considering the results of the chromium analyses, none of the plants composing the natural flora can be described as hyper accumulator plant species (Brooks et al 1977). In our study plants of excellent heavy metal accumulating capacity ( the total heavy metal concentration of the plants more than 1000 mg.kg $^{-1}$ dw) with respect to the plant-fraction include only the following (Table 1.):

Table 1. Chromium concentration in plants with excellent heavy metal accumulating capacity from the sedimentation pond system

| **Plant species** | **Total Cr concentration (mg.kg$^{-1}$) Mean (S.D.)** |
|---|---|
| Agrostis root | 2807 (254) |
| Atriplex root | 2376 (347) |
| Aster root | 1765 (288) |
| Beckmannia root | 1462 (278) |
| Bolboschoemus root | 1773 (347) |
| Echionochloa root, rhizome | 2689 (311) |
| Inula root | 1291 (279) |
| Matricaria root | 1367 (352) |
| Phragmites root | 2022 (325) |

The total chromium concentration results of the sediment fall into the ten thousand (12,000-34,000 ppm) range (Table 2.).

Table 2. Chromium concentration in the upper 10 cm layer of the sediment (mg.kg$^{-1}$ dw)

| | **1. pond unit** | **2. pond unit** | **3. pond unit** | **Control area** |
|---|---|---|---|---|
| **Minimum** | 16,600 | 12,597 | 21,600 | 29.6 |
| **Maximum** | 34,300 | 20,000 | 26,721 | 42.2 |
| **Mean** | 25,450 | 16,298 | 24,245 | 35.9 |

This extremely high degree of the chromium concentration multiplies the time demand of the phytoremediation process. Fortunately, it does not endanger the vegetation with lethal phytotoxicity, because of the relatively low concentration of Cr (VI) (Table 3.) and the green plant covering is significant.

Table 3. Total chromium and Cr (VI) concentration of the sediment in the pond units (mg.kg$^{-1}$ dw , S.D. in parenthesis)

| **Pond unit** | **Total Cr** | **Cr (VI)** | **percentage of Cr (VI)** |
|---|---|---|---|
| **1.** | 34.300 (3254.27) | 97 (12.35) | 0.28 |
| **2.** | 20.000 (2978.56) | 129 (28.26) | 0.43 |
| **3.** | 21.600 (3894.59) | 221 (39.57) | 1.02 |

Chromium removing effect of plants cannot be confirm at this stage, owning to the relatively short study period with measurement only for a single growing seasons. However, the major role of plants in absorption of toxic, easy mobilized Cr(VI) seems clear and in a successive intracellular reduction process less toxic Cr(III) is formed.

By 1 $m^2$ and 30 cm depth at autumn, biomass (stem + leaf and root + rhizome, dry weight) of common reed (*Phragmites sp.*) attained 13 kg and accumulated 6-10 g Cr, top biomass (8.2 kg/ 0.3 $m^3$) of sea club rush (*Bolboschoemus sp.*) was measured in summer, with 8-12 g Cr in above- and below ground parts. Biomass of cockspur (*Echinocloa sp.*) and of cattail (*Typha sp.*), 2.8 kg/$m^2$ and 2.6 kg/$m^2$ respectively, and stabilized chromium therein was also considerable.

The rhizomes and the roots of the plants are the main pool of chromium (Table 4.), similarly to the literature data (Chaney 1983, Lakatos et al 1999, Salt et al 1995 and 1998).

Table 4. Chromium distribution in the parts of some plants from the pond system (mg.$kg^{-1}$ dw , S.D. in parenthesis)

| Plants | Leaf | Stem | Root | Rhizome |
|---|---|---|---|---|
| *Agrostis sp.* | 44.40 (8.14) | - | 2100 (218.32) | - |
| *Atriplex sp.* | 28.15 (10.02) | 111.44 (23.41) | 383.60 (34.67) | - |
| *Aster sp.* | 207.50 (25.73) | 97.91 (13.43) | 1765.34 (98.62) | - |
| *Bolboschoenus sp.* | 124.53 (18.39) | 961.66 (54.26) | 1905.94 (87.45) | 1445.26 (101.23) |
| *Echinocloa sp.* | 40.15 (11.21) | 15.43 (4.12) | 842.50 (64.72) | 315.40 (47.38) |
| *Phragmites sp.* | 123.08 (24.24) | 25.86 (5.54) | 2022.21 (112.39) | 215.64 (52.21) |
| *Typha sp.* | 47.61 (9.58) | 3.34 (0.53) | 1921.24 (294.75) | 732.45 (86.63) |

The green covering is given by the presence of the vegetation, while the absorption and reduction of Cr (VI) are realized in the form of Cr (III), consequently the elimination of the toxic form can be evaluated as a more important process than the possibility of the present phytoextractive procedure.

## 4. SUMMARY

Floristically, units of the pond system are characterized by a relative richness of species (56 species). Dominants are common reed, sea club rush, cattail and aster, but weeds are also considerable. Vegetation cover of the pond units is different varying between 85 and 100 %, though the trend for increase of the green carpet is advantageous.

Result of the elemental analysis for heavy metals revealed that none of the plants constituting the natural vegetation can be treated as hyper accumulator plant.

Plants play a prominent role in the absorption of toxic, easily mobilized and available Cr (VI) and its enzymatic reduction to Cr (III). A green cover and the detoxification process of Cr (VI) by plants is suggested to be more important than the present extensive phytoextraction procedure.

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