

# Removal of Cu, Cd, Zn, Ni and Fe from wastewater comparison of three different substrates used in model scaled constructed wetland

Maja ZUPANČIČ JUSTIN<sup>1\*</sup>, Alenka ŠAJN SLAK<sup>2</sup>,  
Tjaša GRIESSLER BULC<sup>3</sup>

## ABSTRACT:

Different wastewaters contain metals that, unlike organic pollutants, are not degradable in the biological treatment system. Primary removal mechanisms can be achieved via sorption with a use of effective sorption media and precipitation processes which have been well demonstrated for metal removal also in wetland environment.

The aim of the study was to test substrates like sand, peat and ceramics waste particles for removal of selected metal ions in a model-scaled constructed wetland (CW). The model comprised three large compartments where sand, peat-sand mixture or ceramics waste particles were exchanged in three successive experiments.

In the compartment filled with sand 99.3 %, 97.8 %, 97.8 %, 97.0 %, and 32.2 % efficiency of metal removal for Cu, Cd, Pb, Zn, and Ni was achieved respectively. Fe leached out of the substrate in this experiment. In the compartment filled with the mixture of peat and sand was the efficiency of metal removal for Zn 99.8 %, Cu 99.3 %, Cd 98.0 %, Pb 97.9 %, Ni 95.8 %, and Fe 28.3 %, while in the compartment with ceramics the treatment efficiency reached for Cu 99.6 %, Pb 98.0 %, Cd 98.0 %, Fe 92.8 %, Zn 52.0 %, and for Ni 12.4 %. The substrates used in horizontal subsurface flow model expressed the capacity of efficient metal reduction from wastewater and indicate on the possibility of their application in a real-scale CW as a separate, cost-efficient pre-treatment or post-treatment step in the case of additional need of metal removal from the wastewater.

## KEY WORDS:

Constructed wetland, Sand, Peat, Ceramics, Heavy metal, Substrate, Wastewater treatment

Received: 8. 5. 2007.

Accepted: 2. 8. 2007.

<sup>1</sup> Maja Zupančič Justin  
Limnos Ltd., Company for Applied  
Ecology, Water Ecology Group,  
Podlimbarskega 31, SI - 1000 Ljubljana,  
Slovenia  
E-mail: maja@limnos.si

\* corresponding author

<sup>2</sup> Alenka Šajn Slak  
Limnos Ltd., Company for Applied  
Ecology, Water Ecology Group,  
Podlimbarskega 31, SI - 1000 Ljubljana,  
Slovenia

<sup>3</sup> Tjaša Griessler Bulc  
Limnos Ltd., Company for Applied  
Ecology, Water Ecology Group,  
Podlimbarskega 31, SI - 1000 Ljubljana,  
Slovenia

## INTRODUCTION

Toxic metals pose a serious threat to the fauna and flora of receiving water. In spite of strict regulations restraining the careless disposal of metal ions, they still emerge in a variety of wastewaters like road runoff, landfill leachate, mine drainage and in the specific industrial runoff (processing, surface treatment like galvanization) [1,2,3]. The common methods for removal of low concentration of metals from wastewaters are either economically unfavourable (e.g., conventional ion exchange, electrolytic or liquid extraction, electrodialysis) or technically complicated (e.g. precipitation, cementation, reverse osmosis) [4]. The cost of adsorptive metal removal process is relatively high when pure sorbents (activated carbon or hydrated oxides) are used [5]. Therefore, there is an increasing trend of substituting pure adsorbents with natural by-products or stabilised solid waste materials. Especially in developing countries, there exists a great need to use low-cost materials in wastewater treatment processes [6]. Recent developments use in situ treatment of metal contaminated soil and water like electrokinetics, phytoremediation, bioprecipitation processes, soil flushing, solidification and stabilization. In general, in situ remedies are often more economically efficient compared with traditional treatment methods.

The aim of this study was to test substrates like sand, peat and waste ceramics particles for metal ions removal from contaminated water in model scale plant used as a base for application in constructed wetland (CW). If successful, these substrates could provide a cost effective alternative. CWs are already widely used in treating different types of wastewater, such as sewage, storm water, highway runoff, industrial wastewater, agricultural runoff, acid mine drainage and landfill leachate [1,5,7,8,9,10,11,12,13,14]. They are ecosystems, which can be successfully manipulated to treat wastewater. Furthermore, when harnessed, the biological, chemical and physical processes that occur in these ecosystems can be beneficial low cost option for civil applications. They are well suited for large volumes of wastewater with low concentrations of metals. The mechanisms for metal removal in wetlands include beside sedimentation a number of other processes that may be significant including filtration by plants, adsorption, biological assimilation, chemical transpiration and volatilization [2,15]. Experiences in the beginning period of CW operation with too low or too high hydraulic permeability showed that the substrate is of key importance in achieving efficient treatment [16]. However, the substrate represents a major expense at the CW construction. In a case of a need of a frequent substrate exchange, or for the purpose of the removal of specific pollutants, like metal ions, the selection of efficient and cost-effective substrate is very important. For the presented study metal removal efficiency was tested in a model-scaled CW filled with different substrates and inoculated with indigenous microbes, without planting with macrophytes. The main objective of the study was to evaluate the efficiency of three pre-selected materials under controlled experimental conditions to identify the most promising for the potential use in the wastewater treatment with the use of CW. Out of a wide range of sorbents which are available as possible filtration media, sand, peat

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and ceramics were selected on the basis of market accessibility and pre-experiment work completed.

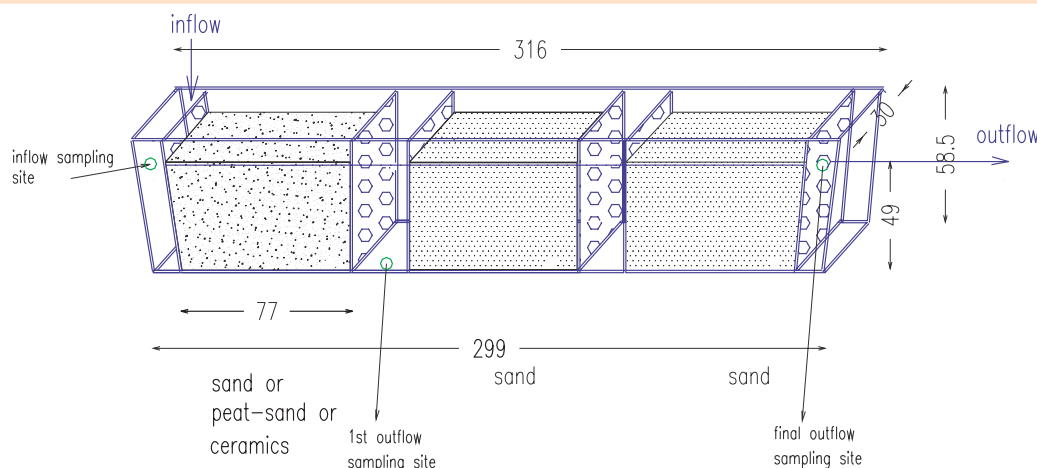
This study follows the simultaneous removal of six different metal ions: Fe, Zn, Cd, Ni, Pb, and Cu as dissolved fractions of these metals often pose environmental concern and were found also in preliminary performed analysis of leachate, highway runoff and industrial wastewater [1,14]. Ni is a naturally occurring element that may exist in various mineral forms. It is used in a variety of applications, including metallurgical and electrical components, such as batteries. Like most metals, the toxicity of Ni depends on the route of exposure and the solubility of Ni compounds [17]. Pb is a natural element, persistent in water and soil. Most Pb in the environment is from anthropogenic sources [18]. Zn is used primarily in galvanized metals and metal alloys, but Zn compounds have also wide commercial applications [19]. Fe is an active metal. It combines with halogens, sulphur, phosphorus, carbon and silicon, and it displaces hydrogen from most dilute acids. Toxicity of Fe to plants is rare, but may occur primarily on acid soils (pH <5.0). Cd occurs predominately in the form of free divalent cations in most well-oxygenated, low-organic-matter and freshwaters [20]. However, particulate matter and dissolved organic matter can bind Cd in biologically unavailable forms. Aquatic organisms are able to bioaccumulate Cd. Cd is a highly toxic metal with no known nutrient properties. It is toxic to a variety of mechanisms in numerous tissues. Cu occurs in natural waters primarily as a divalent cupric ion in free and complexed forms [20]. Cu is a micro nutrient for both plants and animals at low concentrations, but at concentrations only slightly higher, it is toxic to aquatic life. The largest anthropogenic releases of Cu into the environment result from mining operations, agriculture, solid waste and sludge from sewage treatment plants.

## METHODS

A model-scaled wetland – 58.5 cm high, 30 cm wide, with the bottom length of 299 cm and the upper length of 316 cm, without vegetation was placed in an unheated laboratory hall (Figure 1). The measured

**Figure 1.**

The model-scaled wetland divided into seven compartments, filled with sand, peat and ceramics particles.



daytime temperature range was between 6.9 °C and 20.6 °C through the experiment, following the external environmental conditions. The model was divided into seven compartments, separated by six perforated walls. Three large compartments (77 cm long) were filled with substrate up to 49 cm.

Three successive experiments were carried out. In all three experiments, the last two compartments were filled with sand (1 mm – 4 mm diameter size). In the first compartment, sand (Experiment A: sand/sand/sand), peat-sand mixture (Experiment B: peat-sand/sand/sand) and ceramics (Experiment C: ceramics/sand/sand) were exchanged in each experiment. Small compartments (20 cm – 25 cm) were not filled with substrate in order to carry out the sampling for water analyses.

Sand was included for three main reasons. Sand is frequently used substrate in CW so the current study can provide data for comparison with other two substrates, as well as sand filtration has been commonly used for storm water filtration, with similar characteristics as prepared water in our case (low BOD<sub>5</sub> content and presence of metal ions). Washed sand (1 mm – 4 mm diameter size) was obtained from a gravel pit Hotič, Slovenia.

Peat was used on the basis of obtained results from leachate treatment in CW, where higher treatment efficiency had been achieved with additions of peat to the sand substrate compared to treatment beds filled only with sand substrate [8]. Additionally, peat was chosen as an organic material with different natural properties than sand and ceramics, with high cation exchange and sorption capacity.

Sphagnum peat, prepared for horticultural application, without additions of fertilizers or lime, with pH ranged between 4.0 – 4.5 and fibre size between 0 mm – 200 mm was used in a mass ratio 1:3 mixture with sand.

Ceramics was selected as an economically accessible substrate, as waste particles from the ceramics production were used, obtained from the ceramics works Keramika Liboje. Waste porous ceramics particles (size of pore 0.2 μm) were broken by hand into small pieces (1 mm – 8 mm) and washed to eliminate finer material.

Before the start of each experiment, sewage with water addition (1:1) was run through the model for seven days to establish the bacterial population in the fresh substrate, to simulate conditions in CW treating sewage. The dilution was made in order to avoid clogging in the substrate. After substrate inoculation with indigenous micro flora from sewage, prepared artificial wastewater polluted by metals was run through the model for five days in each experimental case. The required concentrations of Cu, Ni, Pb, Zn, Fe and Cd were obtained by step-by-step diluting their commercial stock solutions at 1000 mg/L in HNO<sub>3</sub> to the desired concentrations of 2.5 mg/L for Cu, Ni and Pb; 10 mg/L for Zn and Fe, and 0.5 mg/L for Cd. As a bacterial nutrient source sugar was added in 1 % concentration. The artificial wastewater was supplied with 0.1 L/min flow from a 200 L container positioned above the inflow level

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into the model enabling gravitational flow through the model. Figure 1 shows the inflow and the outflow positions in the model and the sampling points. The water flow in the model was sub superficial.

An analysis of physical and chemical parameters in sewage of the pre-experimental stages and in prepared artificial wastewater were performed. Before the start of each experiment, a sample of sewage was taken at the final outflow of the model for the analyses of metal content, temperature, pH, dissolved oxygen and specific electric conductivity (G). Samples for the same analyses of artificial wastewater were taken at the inflow, and during five days of the experiment at the outflow from the first compartment (first outflow) and at the final outflow from the model (Figure 1) during each experiment. Temperature, pH, G and oxygen content were measured on site, using the MultiLine P4 portable universal pocket-sized meter with the pH combined electrode, SenTix 41 integrated temperature probe, Cellox 325 dissolved oxygen probe and TetraCon 325 standard conductivity cell. Samples for metal analyses were collected in plastic bottles and frozen. 1 mL suprapur HNO<sup>3</sup> per 1 L of sample was added immediately after sampling. Before the analyses, the samples were thawed to room temperature and filtered through white ribbon. All analyses were performed with flame atomic adsorption spectrometry (FAAS), Varian Specter AA 110 (Mulgrave, Victoria, Australia). Cu, Zn, Cd and Pb were determined in the air-acetylene flame, whereas Fe and Ni in the N<sub>2</sub>O-acetylene flame. Standard solutions were prepared from stock standard Cu, Ni, Fe, Cd, Zn and Pb solutions in the concentration of 1,000 ± 2 mg/L (Merck, Darmstadt, Germany).

## RESULTS AND DISCUSSION

During five-day flow of artificial wastewater in all three experiments, pH ranged between 6.5 and 7.8 (Table 1). Compared to the inflow values, a slight decrease in 0.5 – 1 pH was noticed at both outflows in all three experiments. The decrease of pH could be due to microbial degradation of organic matter in anoxic conditions. The decrease could be in part due to the exchange of metal ions for hydrogen ions on the substrate surface. Eger [3] reported a decrease of about 0.1–0.2 pH units at the outflow after the flow of mine drainage through the wetland treatment cell filled with peat substrate. In general, CWs have buffering capacities, which means that the outflow pH remains in the range of neutral limits irrespective of the inflow pH [16]. A similar situation was found in our model where the average pH was 7. At neutral pH we can expect mainly the processes like adsorption of metals, chelate formation and ion exchange on the chosen substrate [3].

There were distinctive differences found in the concentration of dissolved oxygen in the model comparing inflow and outflow tares (Table 1). At the beginning of the artificial wastewater flow, the concentration of dissolved oxygen in the inflow compartment was high (7.9 mg/L on average) and it immediately dropped after the percolation through the first compartment filled with the substrate and stabilized in the other parts of the model at 1.0 mg/L on average. Dissolved oxygen from the inflow water was imme-

**Table 1.**

Parameters measured at the outflow during pre-experimental stage with sewage (Sewage) and in the prepared artificial wastewater at the beginning (Inflow) and during five days of water percolation through the model (1<sup>st</sup> outflow, Final outflow) of each experiment.

**EXPERIMENT A**

Parameter	Unit	Sewage	Inflow	1 <sup>st</sup> outflow	Final outflow
Temperature	°C	16	17	17.5	17.4
pH		7.8	7.5	6.5	6.7
Dissolved oxygen (O <sub>2</sub> )	mg/L	1.63	6.4	1.37	1.05
G	μScm	626	310	646	662

**EXPERIMENT B**

Parameter	Unit	Sewage	Inflow	1 <sup>st</sup> outflow	Final outflow
Temperature	°C	13	11.9	8.8	6.9
pH		7.4	7.2	6.5	6.7
Dissolved oxygen (O <sub>2</sub> )	mg/L	0.81	8.41	1.34	0.56
G	μScm	1177	490	1711	1793

**EXPERIMENT C**

Parameter	Unit	Sewage	Inflow	1 <sup>st</sup> outflow	Final outflow
Temperature	°C	18.2	18.1	20.5	20.6
pH		7.5	7.3	6.7	6.7
Dissolved oxygen (O <sub>2</sub> )	mg/L	2.89	8.94	1.02	0.85
G	μScm	822	457	539	1740

diately incorporated into the degradation processes. Similar low concentration of dissolved oxygen could be found in water at the outflow from CW with horizontal subsurface water flow [16].

The inflow specific electric conductivity (G) of prepared artificial wastewater ranged between 310 μS/cm and 490 μS/cm (Table 1). Upon the percolation of artificial wastewater through the substrate, the G increased in all three experiments and it ranged between 539 μS/cm and 1,793 μS/cm at the outflows. A positive correlation was found between higher G and leaching of Fe ions from the sand substrate.

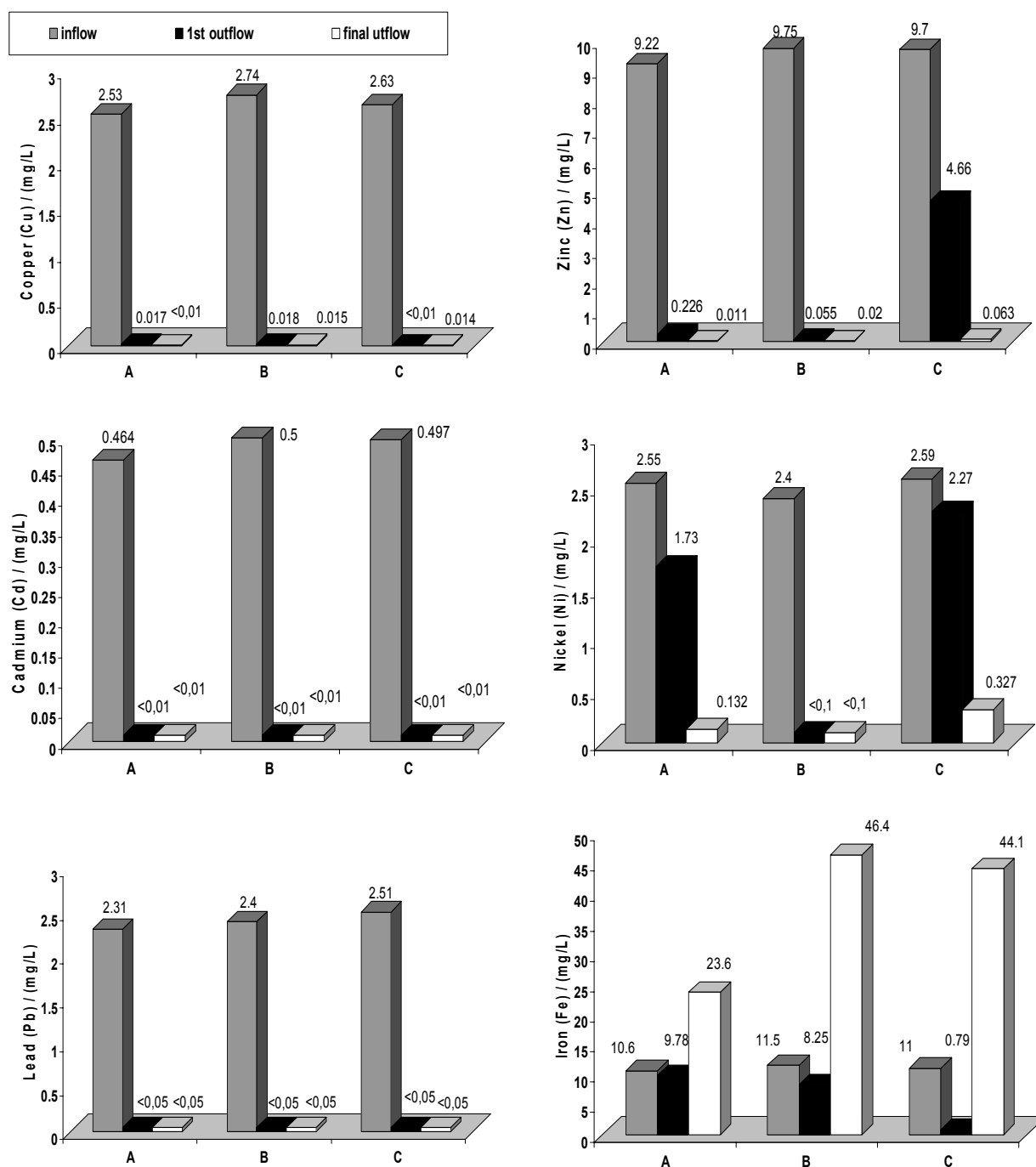
Before the beginning of each experiment, the concentration of metal ions was analysed at the outflow during sewage flow through the model in the pre-experimental stage of each experiment. The results are presented in Table 2. Figure 2 represents the concentrations of metal ions in prepared wastewater at the inflow and at the first and final outflow from the model after five days of artificial wastewater percolation through the model in each experiment. The efficiency of Cu removal was very high in all three tested substrates already in the first compartment (sand 99.3 %, peat-soil mixture 99.3 %, ceramics 99.6 %). In

**Table 2.**

Concentration of metals present in sewage of the pre-experimental stage expressed in mg/L.

Experiment	Cu	Zn	Cd	Ni	Pb	Fe
A	0.053	0.328	<0.01	0.119	<0.05	1.69
B	<0.01	0.098	<0.01	<0.1	<0.05	3.01
C	0.011	<0.005	<0.01	<0.1	<0.05	0.435

the whole model, the efficiency was even higher: Experiment A 99.6 %, B 99.5 % and C 99.5 % (Figure 2). Nearly all Cu was retained already in the first compartment of the model. High efficiency in Zn removal was achieved already after the flow through the first compartment filled with sand (97.6 %) and with the mixture of peat and sand (99.4 %) (Figure 2).



**Figure 2.**

Metal concentrations in the prepared wastewater at the beginning of the experiment (inflow) and after five days of water percolation through the first compartment (1<sup>st</sup> outflow) and through the whole model (final outflow) in three experiments: A (sand/sand/sand), B (peat-sand/sand/sand), C (ceramics/sand/sand).

Lower efficiency of Zn removal was achieved with the use of ceramics (52.0 %). In the whole model, the efficiency of Zn removal was high: Experiment A 99.9 %, B 99.8 % and C 99.4 %. The efficiency of Cd reduction in the first compartment was always high regardless of the used substrate (sand 97.8 %, peat-sand mixture 98.0 % and ceramics 98.0 %) and it remained high at the final outflow from the model: Experiment A 97.6 %, B 98.0 %, C 98.0 %. The concentrations in all measured samples were always <0.01 mg/L. Similar low outflow concentrations in all measured samples were found for Pb (<0.05 mg/L). The efficiency of Pb reduction after the flow of the artificial wastewater through the first compartment was high regardless of the used substrate (sand 97.8 %, peat-sand mixture 97.9 % and ceramics 98.0 %) and it was identical to the efficiency achieved in the whole model: Experiment A 97.8 %, B 97.9 %, and C 98.0 %. Therefore, all Pb was retained already in the first compartment. High removal efficiency of Pb was expected as it is an element primarily associated with suspended solids in wastewater, which are expected to be satisfactorily removed during pre-treatment stage of CW treatment (settling). Low efficiency of Ni reduction in the first compartment was achieved with the use of sand (32.1 %) and ceramics (12.4 %). With the use of peat-sand mixture the efficiency reached 95.8 %. High Ni removal efficiency obtained through the use of peat as a substrate was reported by Eger [3]. The removal of Ni was efficient in the whole model: Experiment A 94.8 %, B 95.8 % and C 87.4 %. The inflow Fe concentration of artificial wastewater ranged between 11.5 and 10.6 mg/L. With the percolation of artificial wastewater through the first compartment, efficient removal of Fe was achieved just by the use of ceramics substrate (92.8 %) (Figure 2). The use of sand and peat-sand mixture showed lower efficiency in Fe removal, 7.7 % and 28.3 % respectively. Leaching of Fe was detected in the whole model. The concentrations of Fe were even higher at the outflow from the model than at the inflow of prepared artificial wastewater. It was evident that sand substrate represented a source of Fe, from which Fe leached out in anoxic conditions of the compartments.

The chemical behaviour and solubility of Fe is strongly dependent upon dissolved oxygen concentrations that exist within the water column and substrate layer. Anoxic (reduced) waters and substrates would likely be dominated by Fe<sup>2+</sup> (soluble ferrous hydroxides – Fe(OH)<sub>2</sub>) rather than by Fe(OH)<sub>3</sub>, insoluble solid phase present in oxygenated environment [21]. Considerable part of Fe increase at the outflow can be attributed also to the interactions with other metals present in the artificial wastewater, where exchange of Fe occurred with other metal cations in the solution. The initial concentration of Fe in sewage was also relatively high compared to other metal concentrations (Table 1), as well as inflow concentrations of Fe in the artificial wastewater.

The used mixtures of substrates in the model expressed the capacity of efficient metal reduction from wastewater with the exception of Fe. The majority of metal ions were eliminated already in the first compartment of the model (Table 3). In the compartment filled with sand, the efficiency of metal removal was as follows: Cu (99.3 %) > Cd=Pb (97.8 %) > Zn (97.0 %) > Ni (32.2 %) > Fe, where Fe leached out of the

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**Table 3.**

Efficiency (%) of metal reduction after the artificial wastewater flow through the first compartment of the model in three successive experiments with sand, peat-sand and ceramics used as a substrate.

Experiment	Sand	Peat / Sand	Ceramics
Copper (Cu)	99.3	99.3	99.6
Zinc (Zn)	97.0	99.8	52.0
Cadmium (Cd)	97.8	98.0	98.0
Nickel (Ni)	32.2	95.8	12.4
Lead (Pb)	97.8	97.9	98.0
Iron (Fe)	-	28.3	92.8

substrate. In the compartment filled with the mixture of peat and sand, the efficiency of metal removal was: Zn (99.8 %) > Cu (99.3 %) > Cd (98.0 %) > Pb (97.9 %) > Ni (95.8 %) > Fe (28.3 %). In the compartment with ceramics particles, the efficiency of metal removal was: Cu (99.6 %) > Pb (98.0 %) > Cd (98.0 %) > Fe (92.8 %) > Zn (52.0 %) > Ni (12.4 %). Generally, the lowest reduction efficiency of the selected substrates was achieved for the Ni ion. Ho et al. (22) achieved efficient Ni reduction using Sphagnum peat. High Ni removal (90 %) with the loading rate of 2 mg/L was reported by Eger (3) with ion exchange on peat medium. Crites et al. [2] also reported difficulties in Ni removal in CW with open water surface and good efficiency for Cu, Pb and Zn reduction. Zn and Ni are among others the most mobile heavy metals in soil and ground water [23]. Furthermore, a mixture of metal ions was used in our experiments and their interactions affect their adsorption and precipitation capacity. Tests on bacterial exopolysaccharide for the evaluation of the uptake capacity of Pb, Cd and Zn showed that competition exists for the same binding sites between Zn and Cd [24]. Further, in the case of peat, two mechanisms of Pb and Zn cations capture were found out. Pb was specifically bounding on active sites of peat surface, while Zn was subjected to unspecific adsorption.

Metal ions in prepared artificial wastewater used in our experiment were present as cations when entering the substrate pore water. Several reactions can take place immediately after the addition of artificial wastewater to the substrate. Metal may complex with other inorganic or organic ions in substrate pore water and thus reduce the concentration of soluble metal ions [25]. Simultaneously, solution metal concentrations may decrease through adsorption or precipitation processes. Adsorption processes are due to an electrostatic bond between the metal and the charged surfaces in substrate. Substrate surface charge is highly depended on pH, with greater negative charge at higher pH. Thus, cationic metals are sorbet most strongly at high pH [25]. Metal cations are removed from solution by precipitation reactions which form new solid phases, usually in association with a corresponding anion already present in the solution [25].

In our experiments, all three sorts of reactions of metal concentration reduction were present. Based on different sorts of substrate and their physical and chemical characteristics, the mechanism of reduction was different among substrates. The major part of complex formation and adsorption processes probably took part in peat substrate with the highest portion of charged surfaces. Peat was followed by sand substrate with

Based on different sorts of substrate and their physical and chemical characteristics, the mechanism of reduction was different among substrates.

higher pore water volume as at the ceramics particles. The crumbled ceramics particles were bigger in size (1 mm – 8 mm) than in sand substrate (1 mm – 4 mm), which most likely caused higher hydraulic conductivity in the compartment filled with ceramics. Shorter retention time together with lower pore water volume in the experiment with ceramics result in low Zn and Ni removal efficiency. Adsorption reactions exhibit time-dependent reaction rates [25]. The longer the metal is in contact with soil, the greater is the strength of the bond formed. This increasing strength of bond may be due to diffusion of metal into micro pores on the substrate surface, and there are suggestions that the rate of reaction is metal-specific. Therefore, the rates are as follows:  $Cd < Mo < Zn < Ni$  [25,26]. The same order of precedence ( $Cd < Zn < Ni$ ) in metal removal efficiency was noticed in our experiments using sand and ceramics.

## CONCLUSION

As regards the tested substrates, we can conclude that the peat-sand mixture expressed the highest efficiency of metal removal. It was followed by sand and ceramics, which expressed lower capacity in Ni and Zn removal. In this experiment, waste ceramics particles were used, which pointed to the possibility of efficient application of different waste materials in removal of metal ions from wastewater. Similar results with nearly complete metal retention in the first parts of CW were found also by Obarska-Pempkowiak [27], Vymaza and Krasa [28] and Cheng et. al. [29].

The present study provides evidence that tested treatment system can be used efficiently in removal of metal ions already in the stage without addition of plants. Nearly all metal ions were retained in the first compartment of the model, thus metal depositions may be removed by exchanging the substrate in the first smaller beds of CW as these processes are limited by the amount of available exchange sites in the substrate and by the transport of contaminants to these sites.

The results of Fe leaching from the sand substrate directed us towards the need of preliminary testing the substrates meant for the use in CW to avoid leaching in case of its high concentrations in wastewater. Fe is for example a common constituent of municipal landfill leachate or mine drainage, which, when exposed to oxygenated aquatic environments, settles out of the water column to form a thick flock on the underlying layer. This can cause substrate clogging, has a negative influence on microbial activity and results in reduced treatment efficiency of the wetland system. For example, pre-treatment system in the form of easily exchangeable substrate-beds or sedimentation ponds could be incorporated into site designs as a means of minimizing iron levels before wastewater is discharged to a CW.

## Acknowledgements

Financial support for this research was provided by the Ministry of Education, Science and Sport, Republic of Slovenia, within the Project on Circulation of Toxic Compounds in Different Substrates of Constructed Wetlands (Project L2–1536).

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