START-UP PERFORMANCE OF CONSTRUCTED WETLAND MICROCOSMS FOR ELECTROPLATING WASTEWATER POLISHING

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ABSTRACT
Two experimental systems which mimic full scale vertical flow constructed wetland were established to study their feasibility to polish electroplating plant effluent. Each system consists of vertical flow PVC columns (80 cm height, 20 cm diameter) filled up to 63,5 cm (20 L) with either mineral or organic media. The systems were fed with either real or synthetic electroplating wastewater containing Zn, Cu, Ni, Fe, Al, and cyanides. Six different configurations (each in duplicate) were selected for the experiment based on flow mode, type of bed media (and presence or absence of vegetation (*Phragmites australis*). The main objective of the system design was to promote metals removal by precipitation as metal sulphides mediated by sulphate reducing bacteria (SRB), which, in general, are obligate anaerobes. Thus, most of the columns are strictly anaerobic. However, also aerobic processes were reported to be efficient for removal of metals and cyanides. Therefore, selected columns of the experimental system are operated as intermittently anaerobic and aerobic. The treatment efficiency after nine-week start-up period of the system operation is as follows: at least: 99% removal of Al, 98% removal of Cu, 89% removal of Ni, 80% removal of Zn (in continuous flow columns), 20% removal of Zn in batch columns, 40% removal of Fe (Fe was released from the batch columns with sand). The effluent concentrations Mn and Fe increased comparing to the influent concentrations. The remarks on the nine-week start-up period of the system operation and the scope of the system application are presented.

KEYWORDS
compost; constructed wetlands; electroplating wastewater; metals; vertical flow

INTRODUCTION

The electroplating wastewater contains chiefly residual metals, cyanides and solvents. Because of its toxicity electroplating effluent belong to a category of waste streams, which are one of the most cumbersome in treatment and acute for the environment. It is a common practice to treat (to various extent) electroplating wastewater before its discharge into sewer system by the physical-chemical processes including chemical precipitation, electrolysis, reverse osmosis, and ion exchange (U.S. EPA, 1998). It is noteworthy that conventional primary and secondary unit processes at municipal wastewater treatment plants are not fully adequate for efficient removal of heavy metals and the other contaminants of electroplating origin. High concentrations of toxic pollutants in the electroplating effluents prevent the application of biological methods for their treatment. Thus, constructed wetlands are not an alternative to conventional physical-chemical methods of electroplating wastewater treatment. However, constructed wetlands may serve as a low cost add-on to conventional treatment of electroplating wastewater prior to its discharge into receiving waters.

In the long-term perspective they can remove the marginal concentrations of heavy metals that cannot be removed by classical physical-chemical methods and they may serve as a suitable risk mitigation strategy in case of failure of the upstream treatment facilities (Diels et al., 2003).

The concept of using constructed wetlands for cost-effective and energy-efficient treatment of industrial wastewaters in the world has been demonstrated with a high degree of success (exhaustive overview is provided by Kadlec and Wallace (2009)). Wetlands have a high potential to remove, cyanides and selected solvents, but highly contaminated substrate would need to be treated as a hazardous material for ultimate disposal after a period which can span from a few to hundred years (Eger and Lapakko, 1989; Kadlec and Wallace, 2009; Gessner et al., 2005). The removal of metals in constructed wetlands is dominated by four mechanisms: adsorption, precipitation, absorption by plants and bacteria, deposition of suspended solids. It should be noted that a minor fraction of metals is removed by hydrophytes, which unlike terrestial plants, cannot hyperaccumulate metals. The main role of these plants is to provide organic matter for the biogeochemical processes through die-back and exudation from the roots (Marchand et al., 2010).

Constructed wetlands can effectively remove metals by reducing sulphate to sulphide. Dissimilatory sulphate reduction (mediated by sulphate reducing bacteria (SRB)) and the subsequent precipitation of metal sulphides have been identified as the most important reactions in metal removal from wastewater. Most of the metals react with hydrogen sulphide to form highly insoluble metal sulphides. Sulphate is reduced to sulphide within the anaerobic zones and is stable while within the reduced environment (WERF, 2006). Removal of metals in sulphate-reducing wetlands was reported to follow two mechanisms: the adsorption of metal onto organic matter and the formation of metal-sulphide precipitates. Adsorption onto organic matter appears to much more rapidly than sulphide precipitation. Metals absorbed to organic matter appear to convert slowly to sulphide precipitates (WERF, 2006; Fitch and Burken, 2003). The key requirements for sulphate-reducing systems are: anaerobic conditions (low redox potential), electron donors (simple organic compounds), microbial groups capable of utilizing inorganic sulphur compounds as electron acceptors; inorganic sulphur compounds (as electron acceptors) (Younger et al., 2002; PIRAMID, 2003; Reddy and DeLaune, 2007). In freshwater wetlands, sulphate reduction rates are generally limited by the amount of sulphates. In constructed wetlands, however, sulphate concentration is usually greater because of wastewater loading, and the sulphate reduction rates are mostly dependent on the substrate supply. Therefore, a major factor limiting the application of microbial sulphate reduction to the removal of metals from carbon deficient industrial wastewaters in wetland systems is the availability of carbon and energy sources to drive the process. In constructed wetlands, for sulphate reduction to be effective for treating wastewater, factors which promote the process and sulphide formation must be maximized and destructive factors minimized. First of all, in order to stimulate the sulphate-reducing microorganisms in the case of carbon-deficient effluents, a proper carbon source should be provided to enhance their grow and to cause other bacteria to remove the oxygen from the environment (Kosolapov et al., 2004). In the systems where sulphate-reducing activity is established following sources of carbon can be used: mulch, hay, compost, corn cobs and wood chips. It should be noted that in order to establish a viable passive treatment system for the removal of sulphate, a carbon source (e.g. sucrose) that can be readily utilized by the sulphate-reducing consortia is essential (Lloyd et al., 2004).

The objective of the experiment is to determine the feasibility and efficiency of electroplating wastewater polishing (detoxification) in constructed wetlands. The project will address the following questions: (i) whether it is feasible to polish electroplating effluent and what are the abiotic removal mechanisms of metals active in electroplating plant effluent treatment, and (ii) whether it is feasible to use the constructed wetlands as an emergency wastewater receiver in case of electroplating plant water system failure.

METHODS

Vertical flow constructed wetland mesocosms

Two experimental systems (operated in France, system A, and in Poland, system B) which mimic full scale vertical flow constructed wetland were established to study their feasibility to polish electroplating plant effluent. Each system consisted of vertical flow PVC columns (80 cm height, 20 cm diameter) filled up to 63,5 cm (20 L) with either mineral or organic media. The systems were fed with either real (system A) or synthetic electroplating wastewater (system B) containing zinc (Zn), copper (Cu), nickel (Ni), iron (Fe), aluminium (Al), and cyanides. Six different configurations (each in duplicate) were selected for the experiment based on flow mode, type of bed media and presence or absence of vegetation. Common reed (*Phragmites australis*), emerged rooted hydrophyte, was selected to be planted (4 stems per column) in the vegetated columns as it tolerates broad range of pH (3,7 – 9,0) and anaerobic conditions (WERF, 2006). The main objective of the system design was to promote metals removal by precipitation as metal sulphides mediated by sulphate reducing bacteria (SRB), which, in general, are obligate anaerobes. Thus, most of the columns are designed to be strictly anaerobic (8 of 12 columns in the each system). Anaerobic conditions in the columns are promoted by their construction and operation mode. These columns are operated in an upflow saturated mode with a 10-cm layer of water over the bed media preventing air from penetrating into the substrate. However, also aerobic processes were reported to be efficient for removal of metals and cyanides. Therefore, selected columns of the experimental system are operated as intermittently anaerobic and aerobic (4 of 12 columns in the each system) which is enabled by fill-and-drain operation batch mode. A cycle in this type of columns consists of: filling phase, holding phase and draining phase. During draining phase air is sucked into the bed media thus promoting aerobic transformation until onset of anaerobic conditions as soon as oxygen is depleted. The remarks on the four-month start-up period of the system A operation and the scope of the system application are further presented.

In the experiment the independent variables (input data): (1) concentration of contaminants depending on the extent of treatment in physical-chemical system at the electroplating plant: treated, pretreated and raw wastewater will be used; (2) flow type: saturated upflow or fill and drain mode; (3) various hydraulic retention time in continuous flow reactors, cycle duration in the batch reactors (14 days); (4) bed media: organic (compost or peat) and mineral (gravel and sand); (5) presence of vegetation: planted and unplanted columns.

The bed media were inoculated with SRB by adding cattle manure (system A) or anaerobic sludge (system B) with initial 14-day batch of wastewater to all the columns. The source of carbon for SRB is organic media (peat or compost). Addition of external carbon source (eg. lactate or acetate) will be considered in the further stage of the experiment. It is assumed that the addition of external carbon source may be needed especially for columns filled with mineral media but also for columns filled with highly decomposed organic media, which is a case in long operated constructed wetlands. The addition a carbon source may increase the treatment efficiency in case of temperature drop, which is to be studied.

The above-mentioned independent variables determine dependent variables (output data) which are: effluent composition and abiotic removal mechanisms. The factors regarded as disturbances are: ambient air temperature and precipitation.

The configuration of the experimental microcosm enables simultaneous comparison of the effect of type of bed media, presence of vegetation, operation mode between different types of columns. The other variables (e.g. influent composition or detention time) affecting the system performance will be studied in the further research. Summary of the operation of experimental columns is presented in Figure 1.

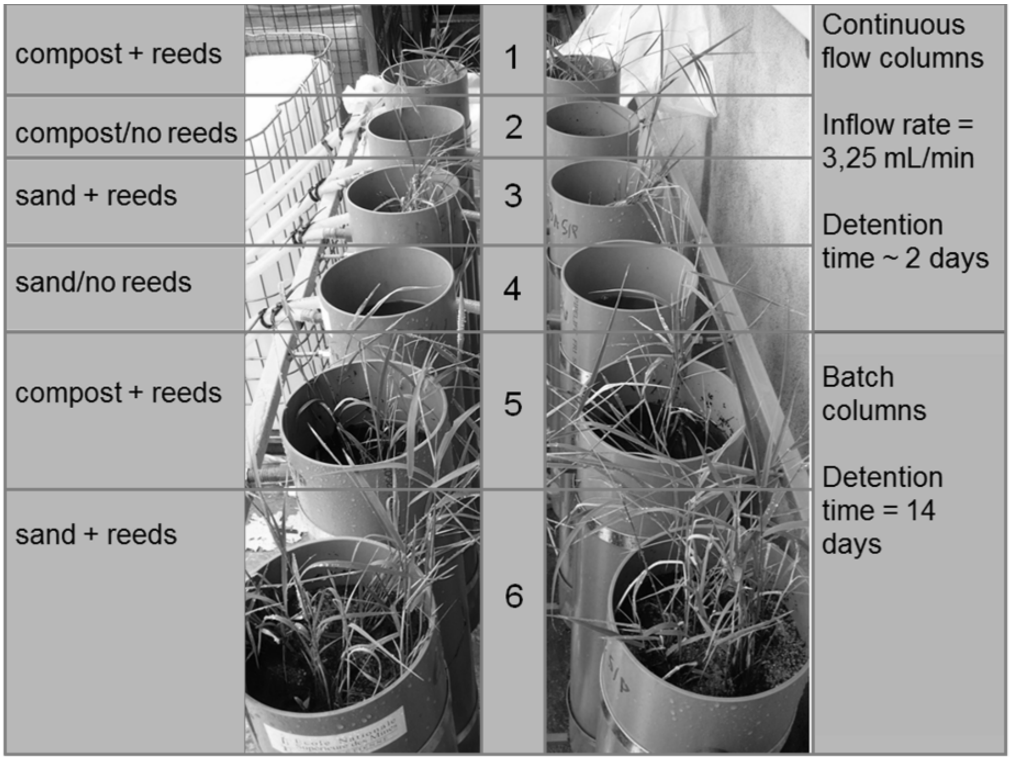

Figure 1 Setup and operation conditions of the microcosm constructed wetland at the initial stage of the experiment

Analytical assays and test methods

Metals were analysed with inductively coupled plasma optical emission spectrometry (ICP-OES) after acidifying the samples with a drop of 65% HNO_3. Concentration of cyanide, phosphate, sulphate and sulphide will be determined by spectrophotometric or chromatographic methods. Determination of COD and BOD will be performed by spectrophotometric method and by the OXITOP method, respectively. Additionally, pH and ORP will be determined for influent, effluent and pore water and at least two sampling depths. Metals forms in wetland media will be studied by sequential extraction procedure based on the Tessier's (1979) method. Mineralogical analyses may be useful in identifying the chemical form of metals retained in the solid phase. Due to the poor crystallinity of the precipitates and/or the relatively low concentrations of metal sulfides few techniques are appropriate for the mineralogical analysis of spent reactive mixtures. Among these methods, scanning electron microscopy equipped for backscattered electron imaging (SEM-BSE) has been the most successful technique, whereas X-ray diffraction or iron Mossbauer analyses have been less effective in detecting amorphous metal sulfides (Neculita, 2008). Both SEM microscopy and X-ray diffraction techniques will be used in this project to study chemical forms of metals retained in the experimental constructed wetlands. Adsorption assays, used to find rates of adsorption and isotherms, will involve widely-accepted and reported methods. Full calibration and check standards as described in Standard Methods (APHA, 2005). Metal sulphide formation rates will be determined in in-situ batch tests. Sulphide formation rates will be found by measuring sulphide concentration in the system effluent.

RESULTS AND DISCUSSION

Removal of metals in vertical flow constructed wetlands microcosms

Influent and effluent quality in terms of metals concentration measured after 9 weeks of the system operation is presented in Table 1 and Table 2.

Table 1. Concentrations of aluminium, copper and nickel in the influent and effluent of the experimental microcosm. The results for the pairs of columns (A and B) were averaged

	Aluminium		**Copper**		**Nickel**	
	Conc. (mg/L)	Removal (per cent)	Conc. (mg/L)	Removal (per cent)	Conc. (mg/L)	Removal (per cent)
Influent	7.039		0.812		0.173	
Effluent						
Columns 1	0.031	99.6	0.023	97.1	0.016	90.8
Columns 2	0.033	99.5	0.011	98.7	0.012	93.3
Columns 3	0.011	99.8	0.019	97.7	0.009	94.9
Columns 4	0.043	99.4	0.046	94.3	0.022	87.2
Columns 5	0.151	97.9	0.011	98.6	0.026	85.1
Columns 6	0.107	98.5	0.010	98.7	0.029	83.0

At the initial stage of system operation it can be observed that Al, Ni, Cu are removed with a very high efficiency (regardless of the type of configuration). Both Ni and Cu form very insoluble sulphides (Sobolewski, 1999). In addition, these metals can be chemically bound to organic material. The probable removal mechanism of Al was precipitation of hydroxide or hydroxysulphate.

The removal of Zn was in the range of 76.2% to 85.2% in the continuous flow columns (1-4) and was significantly lower in the batch columns. The removal mechanism of Zn is assumed to be, as for Cu and Ni, precipitation and sorption.

Currently the removal mechanisms are unknown but it may be assumed that metals are precipitated as sulphides (except Al) or are sorbed in the bed media. It was also observed that Fe was removed with much lower efficiency than Al, Cu, Ni and Zn or was even released from the system. Mn was released from the each type of column. Under anaerobic conditions, manganese is typically quite soluble. Manganese sulphide is stable only at very high pH and high concentration of Mn (II) (Wildeman et al., 1993; Kadlec and Wallace, 2009). Reducing conditions in a constructed wetland matrix conditions promote massive ion release, particularly of Fe and Mn, into the water by reduction of the oxides and oxyhydroxides trapped in the substrate (Goulet and Pick, 2001).

As there was a four-month shift between the start-ups of the systems A and B, the measurements are not available for the system B, whose inoculation with SRB was in progress while the measurements for the system A were performed.

Table 2. Concentrations of zinc, iron and manganese in the influent and effluent of the experimental microcosm. The results for the pairs of columns (A and B) were averaged

	Zinc		**Iron**		**Manganese**	
	Conc. (mg/L)	Removal (per cent)	Conc. (mg/L)	Removal (per cent)	Conc. (mg/L)	Removal (per cent)
Influent	0.123		0.443		0.006	
Effluent						
Columns 1	0.025	79.4	0.426	3.8	0.564	-8725.4
Columns 2	0.029	76.2	0.134	69.8	0.786	-12206.5
Columns 3	0.021	82.6	0.321	27.4	0.043	-579.6
Columns 4	0.018	85.2	0.203	54.1	0.031	-386.7
Columns 5	0.081	34.3	0.249	43.7	0.952	-14794.5
Columns 6	0.114	6.9	0.987	-123.0	0.500	-7723.2

CONCLUSIONS

System performance

The analysis of the performance of the microcosm constructed wetland (system A) after 9 weeks of operation indicates high removal efficiencies of Al, Cu and Ni regardless of the type of the operation mode, bed media, presence of vegetation. Also, high removal efficiency of Zn was observed for continuous flow columns, whereas its retention in the batch columns was markedly lower. Removal of Fe varied in a broad range. Massive release of Mn was observed in all the columns which can be attributed to dissolution of its oxides and hydroxyoxides. Mechanisms affecting removal or release of metals are yet unknown, however of all the hypothesized phenomena will be elucidated in the further research. Various configuration and operation modes applied in the system are expected to create conditions supporting metals sulphides precipitation process to a different extent by this affecting other either synergistic (eg. metals adsorption) or antagonistic (eg. co-precipitation with iron oxyhydroxides) removal processes.

Hybrid system

This research should lead to a set of conditions (flow mode, oxygen conditions, media type, wastewater composition) that can be used to optimize the metal and cyanide removal in electroplating wastewater by constructed wetlands. Based on the literature, it is expected that different oxygen conditions will be advantageous for removal of metals (main objective of this study) and removal of cyanide, organic carbon, nitrogen (depending on its form), phosphorus. Thus, it seems reasonable to assume the final of constructed wetland system for electroplating effluent polishing should combine both anaerobic and aerobic conditions in a hybrid system, whose configuration and operation mode will be established in this research. Marchand et al. (2010) stated that a constructed wetland based on a matrix with exclusively reducing conditions cannot be efficient in the removal of metals. Since, most metals in the precipitate as metal oxides or adsorb onto organic matter at redox potentials higher than 100 mV it is worth considering the design of a system with two separate compartments, i.e., a first compartment to promote sulphate reduction and a second, oxidizing compartment to enhance metal co-precipitation with iron oxides (Dorman et al., 2009).

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