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Polishing of synthetic electroplating wastewater in microcosm upflow constructed wetlands: Effect of operating conditions

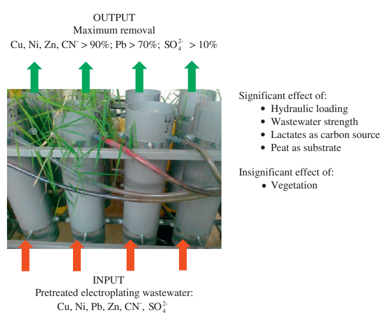
Adam Sochacki [a,b,*], Joanna Surmacz-Górska [a], Olivier Faure [b], Bernard Guy [b]

[a] Environmental Biotechnology Department, Faculty of Power and Environmental Engineering, Silesian University of Technology, ul. Akademicka 2, PL-44 100 Gliwice, Poland
[b] Ecole Nationale Supérieure des Mines, GéoSciences & Environnement Département, CNRS:UMR 5600, EVS; 158, cours Fauriel, F-42023 Saint-Etienne Cedex 2, France

HIGHLIGHTS

- This is the first study on electroplating wastewater polishing in subsurface-flow CWs.
- Upflow columns filled with peat or gravel were used in one-year experiment.
- High removal efficiency can be achieved for Cu, Ni, Zn and cyanides.
- Lactates as external carbon source improve removal of metals.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper addresses the issue of polishing electroplating wastewater in subsurface vertical flow constructed wetland. Electroplating wastewater treatment or polishing in constructed wetlands (CWs) was studied to a very limited degree. Four types of microcosm upflow constructed wetlands were selected for the experiment based on type of bed media and the presence or absence of vegetation (*Phragmites australis*). The main objective of the system design was to promote metals removal by precipitation as sulfides mediated by sulfate reducing bacteria. The experimental system consisted of eight PVC columns (diameter 20 cm) filled up to. 63.5 cm with either gravel or gravel–peat mixture and was operated for one year, polishing synthetic electroplating wastewater. The wastewater used in this study contained metals (Cu, Ni, Pb and Zn), cyanides and sulfates, which typically occur in electroplating wastewater. During the experiment the effect of the following factors was studied: presence of vegetation, hydraulic loading, wastewater strength, type of bed media, and addition of lactates as external carbon source for the columns with gravel. The results showed that the upflow columns can efficiently remove metals (with the exception of Pb) and cyanides. It was observed that the removal efficiency of Cu, Ni and Zn increases with increasing influent concentration of metals and increasing hydraulic loading rate. The role of plants and bed media was minor. The addition of lactates to the feed of the columns with gravel was found to improve the reduction of metals concentration in the passing wastewater.

Abbreviations: COD, chemical oxygen demand; CW, constructed wetland; DW, dry weight; ECS, external carbon source; HLR, hydraulic loading rate; HRT, hydraulic retention time; MAD, median absolute deviation; SRB, sulfate-reducing bacteria; UF, upflow; UF-GP, vegetated upflow column with gravel; UF-GU, unvegetated upflow column with gravel; UF-PP, vegetated upflow column with peat; UF-PU, unvegetated upflow column with peat.

* Corresponding author at: Environmental Biotechnology Department, Faculty of Power and Environmental Engineering, Silesian University of Technology, ul. Akademicka 2, PL-44 100 Gliwice, Poland. Tel.: +48 32 2371169; fax: +48 32 237 29 46.

E-mail addresses: adam.sochacki@polsl.pl (A. Sochacki), joanna.s.gorska@polsl.pl (J. Surmacz-Górska), ofaure@emse.fr (O. Faure), bguy@emse.fr (B. Guy).

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1. Introduction

Electroplating is a process of applying metal coating to an object to enhance its protective properties and alter its appearance, or both [1]. High concentrations of toxic pollutants in the electroplating effluents (metals and cyanides often in hundreds of mg/L [1]) preclude direct application of biological methods for their treatment. Thus, constructed wetlands (CWs) are not an alternative to conventional physical–chemical methods of electroplating wastewater treatment. The term 'polishing' is understood as a treatment of wastewater, pretreated by conventional methods, to the level that allows discharge into sewer or the environment. Thus, the polishing process would be employed to reduce residual amounts of metals and cyanides, which are invariably present in the electroplating wastewater. 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 cyanides of electroplating origin, and the biological processes may be inhibited by these contaminants if the biomass was not previously adapted [2–4]. Moreover, treatment of wastewater containing metals by activated sludge impairs the quality of the excess sludge precluding its agricultural application [5]. Thus, even the polishing of wastewater discharged into municipal sewer should be important from the environmental perspective. The application of CWs for the treatment of electroplating wastewater was reported scarcely in the literature. Ranieri and Young [6] studied the removal of Ni and Cr (and other contaminants) from municipal wastewater containing about 20% of electroplating and textile wastewater. This study consisted in monitoring of a full-scale CW with horizontal subsurface flow. The treatment of electroplating effluents was also investigated in the system with water hyacinth in Asia [7,8]. Vymazal and Kröpfelová [9] referred to the work of Shroff [10] that was dealing to some extent with the treatment of electroplating wastewater. The important feature of metals is that they can only be removed from wastewater but cannot be destroyed. This allows assumption that metals are accumulated in wetland substrate or biota [6]. The removal of metals in subsurface CWs is dominated by four mechanisms: adsorption, filtration and sedimentation, association with metal oxides and hydroxides, and precipitation as sulfides. The extent of these processes depends on the type of the CWs, pH, redox potential, influent composition, the dominant plant species and microbial activity [11]. Since, in general, metal sulfides are less soluble than their carbonate or hydroxide counterparts, this process allows achieving more complete precipitation and stability over a broader pH range [12]. Some of the metals which react with sulfides to form highly insoluble metal sulfides are: Cu, Fe, Ni, Pb, and Zn. These metals are often present in electroplating wastewater [13]. The key requirements for sulfate-reducing systems are: anaerobic conditions (oxidation–reduction potential below −100 mV), electron donors (simple organic compounds), microbial groups capable of utilizing inorganic sulfur compounds as electron acceptors; inorganic sulfur compounds (as electron acceptors) [14–16]. The major factor limiting the application of microbial sulfate reduction to the removal of metals from carbon deficient industrial wastewaters (such as electroplating wastewater) in CWs is the availability of carbon and energy sources to drive the process. In order to stimulate sulfate-reducing bacteria (SRB) in the case of carbon-deficient effluents, a proper carbon source should be provided to enhance their growth and to cause other bacteria to remove the oxygen from the environment [11]. Unlike for natural wetlands, sulfates are not limiting substance in CWs treating industrial wastewater, as sulfuric acid is often used to adjust pH of wastewater [11]. The conditions favorable for SRB may occur in various types of wetland systems, but the upflow (UF) CWs appear viable solution. They are characterized by the fact that their bed is constantly saturated and permanently flooded over the surface. UF CWs are, in fact, mostly applied when anaerobic treatment processes should be promoted, such as bacterial sulfate reduction [17]. Importantly, also cyanides can be degraded under anaerobic conditions in various biotic and abiotic processes [18].

The goals of the experiment were to study the feasibility of polishing electroplating wastewater and to study the effect of hydraulic loading, vegetation, type of bed media, wastewater strength, and addition of external carbon source.

2. Materials and methods

2.1. Microcosm constructed wetlands

The experimental system consisted of eight PVC columns (height, H = 80 cm, diameter, d = 20 cm) filled up to 63.5 cm with either mineral or mixed organic-mineral media. The active bed area (A) corresponding to these dimensions was 0.0314 m^2, the bed volume (V) was 20 L. The columns were operated in a UF saturated mode with a 6.5-cm layer of water above the bed media preventing air from penetrating into the substrate. Thus, water depth (h) in the system was invariably 70 cm and the corresponding nominal wetland volume (V_{nom}) was 22 L. These columns were fed from the bottom by peristaltic pump Masterflex® L/S® 7523-80 using PharMed® BPT tubing (2.79 mm) and the outlet was situated 70 cm above the bottom. The schematic of column used in the experiment is shown in Fig. 1.

The main objective of the system design was to promote metals (Cu, Ni, Pb, Zn) removal by precipitation as sulfides mediated by SRB, which, in general, are obligate anaerobes. Anaerobic conditions in the columns were promoted by their construction and operation mode. The columns were filled with quartz gravel (3–8 mm) or equivolume gravel–peat mixture (hereafter referred to as 'peat'). The inlet zone at the bottom of the columns with peat contained 10-cm layer of the gravel (as shown in Fig. 1). The pH value of the peat was 3.5–4.5; organic matter content 89.9% of DW, and water-holding capacity 746 mL/L. The bed media were inoculated with SRB using anaerobic sludge (mesophilic anaerobic digestion) with initial 14-day batch of wastewater to all the columns prior to the start-up of the experiment. Selected columns were planted with rhizomes of *Phragmites australis* (Cav.) Trin. ex Steud and *Phalaris arundinacea* L. Four types of UF-CWs were selected for the experiment based on type of bed media and the presence or absence of vegetation. Eight columns were used in this study, since each type of column was duplicated. The following types of columns were used:

- columns filled with **p**eat and **p**lanted (UF-**PP**),
- columns filled with **p**eat and **u**nplanted (UF-**PU**),
- columns filled with **g**ravel and **p**lanted (UF-**GP**),
- and columns filled with **g**ravel and **u**nplanted (UF-**GU**).

The experimental system was situated in laboratory conditions in Gliwice, Poland. It was in operation from January, 2012 to January, 2013, which is 53 weeks. The feed of the system was prepared by dissolving salts of metals and sulfates in tap water in a 250-L container. The salts used were $Pb(NO_3)_2$, $NiSO_4 \cdot 6H_2O$, $ZnCl_2$, $CuSO_4 \cdot 5H_2O$, Na_2SO_4. The system was fed with low-strength and high-strength wastewater. The former was fed from January, 2012 to April, 2012, and the latter from May, 2012 to January, 2013. The concentration of sulfates was equal in the both influents at 500 mg/L (resulting from dissolution Na_2SO_4), and the Pb concentration was equal at 1 mg/L throughout the experiment. The final concentration of sulfates was higher (up to 860 mg/L) in the feed because of sulfates in the tap water used. The concentration of Cu, Ni and Zn was raised from 1 mg/L in the low-strength feed to 5 mg/L in the high-strength feed. In week 33 the inflow rate (Q_{in}) to the columns was decreased from 3.25 to 2.00 mL/min. In week 44 of the experiment lactates were started to be added to the influent fed to the columns with gravel (UF-GP, UF-GU). Lactates were added to the feed as 80% lactic acid and the dosage was calculated based on the assumption that a