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Polishing of synthetic electroplating wastewater in microcosm upflow constructed wetlands: Metals removal mechanisms

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

- Microcosm constructed wetlands were examined as sulfate reducing systems.
- Metals binding mechanisms in spent wetland substrate were studied.
- Bacterial sulfate reduction was found to play minor role in metals removal.
- Adsorption and oxic removal processes bind metals in a short-time experiment (53 weeks).
- Short-term studies should not be extrapolated to predict long-term behavior.

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ABSTRACT

This paper presents the study of the metals removal mechanisms in microcosm upflow constructed wetlands used for polishing of synthetic electroplating wastewater. Four types of columns were used: with and without plants and with different bed media (peat or gravel). The main design goal of the columns with peat was to promote precipitation of metals with biogenic sulfides produced by sulfate-reducing bacteria. The feed of the system contained mainly Cu, Ni, Pb, Zn, sulfates and cyanides. The substrate from the microcosm was sampled after cessation of the experiment (53 weeks) from the bottom and top layers of selected columns and was analyzed using sequential extraction procedure and scanning electron microscopy-energy-dispersive X-ray spectroscopy method. Additionally, solids retained on filter surface after filtering water samples withdrawn from the water layer covering the bed media in selected columns were analyzed by the latter method. The obtained results showed that the intended process for metals removal, which was precipitation of metal sulfides, was responsible for binding only a minor fraction of metals. The major portion of metals was present as exchangeable and reducible fraction. The presented study suggests that the onset of the conditions favorable for precipitation of sulfides may not occur during short-term experiment. It may stem from the specific characteristics of the experiment. It is suggested that short-term studies should not be extrapolated to predict long-term behavior of the system.

1. Introduction

The concept of using constructed wetlands (CWs) for cost- and energy-efficient treatment of industrial wastewaters laden with metals has been demonstrated with a high degree of success in the world [1,2]. The application of CWs for the treatment of electroplating wastewater was reported scarcely in the literature. On the Web Of Knowledge [3] a query including 'electroplating' and 'wetland*' (as topics) yielded only 6 results. Five of which dealt with interactions between plants and metals, and one regarding mobility of Cr in natural wetlands. Noteworthy, none of these articles reported application of CWs for the treatment of electroplating wastewater. The challenge of treating or polishing electroplating wastewater in CWs is that it contains high concentrations of metals and cyanides (often on the order of hundreds of mg/L) and is deficient in organic matter [4]. Indeed, the treatment of raw electroplating wastewater appears unfeasible to the toxic effect on the plants and microorganisms and the necessity of frequent

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Abbreviations: bot, bottom; BSE, backscattered electron (detector); CW, constructed wetland; DW, dry weight; EDS, energy-dispersive X-ray spectroscopy; HRT, hydraulic retention time; SEM, scanning electron microscopy; SEP, sequential extraction procedure; 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.

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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exchange of the bed medium due to exhaustion of its sorption properties [5]. Constructed wetlands can be used for the treatment (polishing) of pretreated electroplating wastewater, in which relatively low concentrations of metals and cyanides are present. Metals because of their nature, unlike cyanides or numerous organic compounds, cannot be degraded in CWs to simpler substances. For this reason, the retention mechanism of metallic pollutants is crucial as it determines their mobility in the system [6,2]. The removal of metals in subsurface-flow CWs is dominated by four mechanisms: adsorption, precipitation of metal sulfides or (oxy)hydroxides, and deposition of suspended solids. It should be noted that a minor fraction of metals is removed by hydrophytes, which unlike terrestrial plants, cannot hyperaccumulate metals [7]. Precipitation of metals with biogenic sulfides is the crucial removal process because metal sulfides can remain in the sediments as long as anoxic conditions occur and solubility and mobility is very low as compared to other retention mechanisms [2]. This process is mediated by sulfate-reducing bacteria (SRB), whose growth requires: anoxic conditions, presence of simple organic compounds (as electron donors), sulfates (as electron acceptors) [8,9]. Considering the polishing of electroplating wastewater in CWs it can be stated that the required availability of sulfates can be easily met because this type of wastewater contains elevated concentrations of sulfates (added as sulfuric acid to adjust pH) [10]. Anoxic conditions can occur in the CWs with saturated bed media as horizontal-flow systems or vertical-flow system with saturated bed (e.g. upflow (UF) systems). A proper carbon source should be provided to cause other microorganisms to remove the oxygen from the environment but also to stimulate the growth of SRB [2]. The aforementioned carbon deficiency of electroplating wastewater necessitates the use of organic carbon sources for SRB when this wastewater is to be treated in CWs. Carbon source for SRB can be of internal or external origin. The latter can be added as aqueous solution to the wastewater and the former is present in the system as a solid form. Both types of carbon source can be used in CWs [11]. Constructed wetlands were found to efficiently remove metals by their precipitation with sulfides, but this process is dependent on numerous factors such as: type of wastewater, type of carbon source, retention time and maturity of the system [5,12–14]. The predominant removal mechanisms should be evaluated for a specific case.

The efficiency of CWs for wastewater treatment is often based on influent–effluent comparison, in which the treatment system is regarded as a “black box” [2]. The knowledge of the major removal mechanisms allows prediction of the future performance of a system and its impact on the environment after its operation is terminated. Importantly, the information furnished by the small-scale studies could enhance the design of large-scale system by emphasizing those features of a system that promote the dominance of the most advantageous mechanism of removal.

The goal of the experiment presented in this paper was to study the removal mechanisms of metallic pollutants in microcosm upflow CWs polishing synthetic wastewater. The obtained results were also discussed in light of the treatment efficiency of the microcosm system presented in [15]. The detailed description of the experimental system and the performance results were presented in [15].

2. Methods

2.1. Microcosm constructed wetlands

The experimental system included four types of microcosm upflow CWs depending on the type of bed media and the presence of vegetation: vegetated columns with an equivolume mixture of peat and gravel (hereafter ‘peat’) (UF-PP columns), unvegetated columns with peat (UF-PU), vegetated columns with gravel (UF-GP) and unvegetated columns with gravel (UF-GU). Each type of column was duplicated, therefore 8 columns were used in total. The goal of the columns with peat (UF-PP and UF-PU) was the removal of metals by their precipitation with biogenic sulfides produced by SRB. Peat was used to serve as a carbon source for SRB on the assumption of its hydrolysis and fermentation to produce compounds utilized by SRB (e.g. acetates or lactates). The columns with gravel were used a reference systems, to which no carbon was added, neither as solid material (e.g. peat) nor dissolved substances present in the feed, before week 44 of the experiment. In week 44 lactates were added to stimulate SRB in the gravel columns and to compare the effect of internal (peat) and external (lactates) carbon source on the performance of the microcosm CWs. The feed with lactates were added only to the gravel columns. The electron acceptor for SRB was sulfates present in the feed. The columns were fed for 53 weeks (the whole experiment) with synthetic electroplating wastewater. In the end of the experiment the substrate from the columns was analyzed to elucidate metal removal mechanisms. The composition of the feed was modified during the experiment and was presented in detail in [15]. The median composition of wastewater (with minimum–maximum values in the brackets) for the whole experiment (53 weeks) was as follows:

- For the feed without lactates: Cu 1.23 mg/L (0.16–20.58 mg/L), Ni 5.00 mg/L (0.99–6.75 mg/L), Pb 0.67 mg/L (0.28–3.95 mg/L), Zn 3.65 mg/L (1.20–16.80 mg/L), cyanide 1.04 mg/L (0.425–5.99 mg/L), sulfate 850 mg/L (720–855 mg/L);
- For the feed with lactates: Cu 2.65 mg/L (0.98–4.86 mg/L), Ni 5.83 mg/L (4.77–6.58 mg/L), Pb 0.78 mg/L (0.50–1.29 mg/L), Zn 6.27 mg/L (5.38–7.26 mg/L), cyanide 1.28 mg/L (0.40–5.69 mg/L), sulfate 855 mg/L (700–935 mg/L).

The feed without lactates was used during the whole experiment (weeks 1–53) as the influent of the columns with peat and in weeks 1–43 as the influent of the columns with gravel. In weeks 44–53 the feed with lactates was used as the influent of the columns with gravel. The results presented in this paper are for the planted columns with peat (UF-PP), planted columns with gravel (UF-GP), and to lesser extent for the unplanted columns filled with gravel (UF-GU). The UF-PU columns will not be further discussed in this article.

2.2. Sampling procedure

Substrate samples were taken from the bottom and top of columns after cessation of the experiment (53 weeks). It was assumed that these zones were represented by 150 mm layer from the bottom or top surface. The samples were than homogenized and subdivided into the subsamples for sequential extraction procedure (SEP) and scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) analyses. The additional samples were: filters through which water layer over the bed medium of the UF-GU and UF-PP columns were filtered. To this end 1.5 L wastewater was withdrawn from the water layer of the UF-PP and UF-GU columns and was filtered through a 0.45 μm filter.

2.3. Sequential extraction procedure

The manner in which metals were bound to substrate in the experimental system was assessed by the SEP based on the BCR2 protocol [16]. This procedure consists of three steps devised to extract three operationally defined fractions. In the first step exchangeable, water- and acid-soluble fraction was targeted and 0.11 M acetic acid was used. The second step was to extract