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Distribution and mass balance of hexavalent and trivalent chromium in a subsurface, horizontal flow (SF-h) constructed wetland operating as post-treatment of textile wastewater for water reuse

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ABSTRACT

In this study, during a two-year period, we investigated the fate of hexavalent and trivalent chromium in a full-scale subsurface horizontal flow constructed wetland planted with *Phragmites australis*. The reed bed operated as post-treatment of the effluent wastewater from an activated sludge plant serving the textile industrial district and the city of Prato (Italy). Chromium speciation was performed in influent and effluent wastewater and in water-suspended solids, at different depths and distances from the inlet; plants were also analyzed for total chromium along the same longitudinal profile. Removals of hexavalent and trivalent chromium equal to 72% and 26%, respectively were achieved. The mean hexavalent chromium outlet concentration was $1.6 \pm 0.9\,\mu g\,l^{-1}$ and complied with the Italian legal limits for water reuse. Chromium in water-suspended solids was in the trivalent form, thus indicating that its removal from wastewater was obtained by the reduction of hexavalent chromium to the trivalent form, followed by accumulation of the latter inside the reed bed. Chromium in water-suspended solids was significantly affected by the distance from the inlet. Chromium concentrations in the different plant organs followed the same trend of suspended solids along the longitudinal profile and were much lower than those found in the solid material, evidencing a low metal accumulation in *P. australis*.

1. Introduction

Textile wastewater contains great amounts of a number of toxic and recalcitrant chemicals and its treatment is therefore of great environmental importance. Moreover, textile districts consume large quantities of water thus producing high volumes of wastewater. Consequently, for textile manufacturing processes more than for other kind of industrial productions, a wastewater management system capable of guaranteeing water reuse is of paramount importance. Typical contaminants of textile effluents are organic compounds and solvents used for dyeing polyester fibres, reducing agents and sulphate salts employed as additives in dye baths, and heavy metal complexes with azo-dyes that are used for dye fixation in wool [1]. In this last process, one of the most representative heavy metals is chromium.

In aquatic environments chromium can be present as Cr(III) and/or Cr(VI), mainly depending on pH and redox conditions; the two forms behave quite differently, since Cr(III) is much less soluble and therefore less mobile than Cr(VI).

The toxicity of chromium is highly dependent on its oxidation state; in fact, the hexavalent form is known to be toxic for many plants, animals and microorganisms, and clear evidence indicates that exposure to certain levels of Cr(VI) can result in significant risks for human health [2–4]. Conversely, the trivalent form is significantly less harmful and is an essential trace nutrient in the human diet [5,6]. According to these facts, limits for water reuse of $100\,\mu g\,l^{-1}$ and $5\,\mu g\,l^{-1}$ are enforced by the Italian regulation [7] for total and hexavalent chromium, respectively.

The heavy metal removal efficiency of SF-h constructed wetlands (CWs) has been monitored by different authors in full-scale systems and in pilot plants fed with real wastewater, both of domestic and industrial origin, evidencing good performances for several elements, including chromium [8–13]. Regarding plant chromium uptake in CW, few papers are currently present in literature and their results suggest that the actual phytoextraction efficiency is poor [10,14,15]; these papers also investigated the chromium vertical and horizontal distribution in SF-h systems. However, in all these studies, hexavalent chromium was not

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