Total and hexavalent chromium removal in a subsurface horizontal flow (h-SSF) constructed wetland operating as post-treatment of textile wastewater for water reuse

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ABSTRACT

In this study we investigated total and hexavalent chromium removal in an h-SSF constructed wetland (CW) planted with Phragmites australis and operating as post-treatment of effluent wastewater from an activated sludge plant serving the textile industrial district of Prato (Italy). Two measurement campaigns were carried out in 2006 and 2008–2010 in which more than 950 inlet and outlet samples were analyzed. When inlet and outlet concentrations were compared one to the other, the latter were found to be significantly lower than the former \((p < 0.001)\); during the entire period of investigation, removal of hexavalent chromium equal to about 70% was achieved. Outlet concentrations ranged between values lower than the quantification limit \((0.5 \mu g L^{-1})\) and \(4.5 \mu g L^{-1}\), and in all cases were therefore lower than the limit indicated for hexavalent chromium in the Italian regulation for water reuse \((5 \mu g L^{-1})\). The comparison of the removal efficiencies achieved for hexavalent and trivalent chromium during the two campaigns suggested that the removal of the former can be sustained in the long term, while for the latter, the treatment efficiency is more sensitive to the age of the CW, being that it is based on trivalent chromium retention in the reed bed.

Key words | hexavalent chromium, horizontal subsurface-flow constructed wetland, total chromium, water reuse

INTRODUCTION

The treatment of wastewater deriving from textile districts is an issue of great environmental importance owing to the complexity of the removal of chemicals involved in this industrial process, and to their toxicity. Moreover, textile industry consumes a large quantity of water (about 10–50 L are required per kilogram of textile, depending on the type of processing), consequently producing large volumes of wastewater. Therefore, for textile districts more than for other kinds of industry, it is of paramount importance to have a wastewater management system capable of ensuring water reuse. In order to achieve this goal the quality level of the effluent must meet the stringent limits enforced by the Italian regulation for water reuse (Ministerial Decree of the Italian Republic n.185/2003).

One of the chemicals most widely used in the textile industry is chromium, which exists in aquatic environments in either the trivalent Cr(III) or hexavalent Cr(VI) oxidation states. The toxicity of chromium is highly dependent on its oxidation state; in fact, the hexavalent form is known to be toxic to many plants, animals and microorganisms, and several data in the literature indicate that the exposure to certain levels of Cr(VI) can promote cancer development (Nethercott et al. 1994; Wang et al. 1997; Environmental Protection Agency 1998). Conversely, the trivalent form is significantly less harmful and is an essential trace nutrient in the human diet (Anderson 1989, 1997). According to these facts, limits for water reuse of 100 and \(5 \mu g L^{-1}\) are established by the above-mentioned Italian regulation for total and hexavalent chromium, respectively.

Constructed wetlands (CWs) are a simple and low-cost technology that have been extensively used for the treatment of domestic wastewater (especially from small communities) (Kowalik et al. 1995; Brix 1998; Vymazal 2001) and, less frequently, for industrial applications (Knight et al. 1993; Grismer et al. 2005; Del Bubba et al. 2004).

Published literature indicates that CW systems play an important role in improving the quality of wastewater containing chromium (Makos & Hrncir 1995; Scholes et al. 1998; Jin 2004; Ranieri 2004; Lesage 2006; Calheiros et al. 2009; Kröpfo- lova et al. 2009) and could therefore represent a low-cost and environmental-friendly approach to the sustainable management and reuse of chromium-polluted water. However, in most of these studies, only total chromium (CrTOT) was monitored, whereas the behaviour of the hexavalent form of the metal in an h-SSF CW was only investigated by Makos & Hrncir (1995). In their study, the effectiveness of wetland systems for Cr(VI) removal was demonstrated, even if the investigation was carried out on a laboratory scale, using a standard solution of Cr(VI) instead of real wastewater and, above-all, with soil as the filling medium; therefore, the applicability of the results of Makos & Hrncir (1995) to the current wetland technology is highly questionable.

For the purpose of increasing knowledge of CW performance in the removal of total and hexavalent forms of chromium and verifying the feasibility of wastewater reuse within the textile industrial district of Prato (Italy) for which chromium represents the only critical parameter, this paper investigated the removal efficiency of CrTOT and Cr(VI) in an h-SSF CW planted with Phragmites australis (Cav.) Trin. ex Steudel. The CW acted as post-treatment of the effluent from the Baciaca- vallo (Prato) activated sludge plant (ASP), which treats the wastewater produced by the local textile industries.

**MATERIALS AND METHODS**

**Reagents**

The reagents HNO3 65%, and H2O2 30% were purchased from Merck (Darmstadt, Germany) and were all Suprapur® grade. K2Cr2O7 (purity ≥ 99.0%), CrCl3 (purity ≥ 99.99%), CH3COONH4 (purity ≥ 99.99%), CH3COOH 100% (purity ≥ 99.99%), ammonium pyrrolidinedithiocarbamate (APDC) (purity = 99.0%), CHCl3 (purity ≥ 99.0%), Na2CO3 and ICP chromium analytical standard (AA/ICP calibration/check standards for environmental analysis, 1 g L−1) were supplied by Sigma-Aldrich (Milwaukee, IW, USA).

**Description of the study site and the CW**

The textile district of Prato includes more than 250 industries that use water for their processes (dyeing, washing, finishing). Industrial wastewater, together with domestic sewage from the urban area of Prato, run into five centralized ASP managed by GIDA S.p.A. The Baciaca- vallo plant is the largest and receives 38,000,000 m³ year−1 of wastewater, 20,000,000 of which are from industrial sources. The treatment process consists mainly of equalization, primary settlement, biological oxidation, secondary settlement, clarifloculation and a tertiary treatment based on ozone which is activated each week from Monday to Friday.

In order to investigate the ability of wetlands as post treatment technology to increase wastewater quality for its reuse, an h-SSF CW was implemented in 2003. Major design characteristics and management conditions of CW are reported in Table 1. In particular, an inlet flow of about 1 m³ h−1 (corresponding to a hydraulic loading rate (HLR) of 13.5 cm day−1) was applied to the system. The flow was measured using an electromagnetic flow-meter, model PROMAG 50P DN15 (Endress + Hauser, Reinach, Swiss). A requirement equal to approximately 4,500 m³ day−1 of effluent wastewater for reuse is currently estimated in the industrial district of Prato. Based on the HLR adopted in this study, the demand for effluent wastewater could be satisfied with a surface area of about 5.5 ha.

**Wastewater sampling**

Two sampling campaigns were conducted between 2006 and 2010. For both campaigns, 24-h composite wastewater

<table>
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<th>Major design parameters and management conditions of the h-SSF CW</th>
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aAverage value during the monitored period.
bCalculated according to Reed et al. (1995).
samples were collected at the inlet and outlet of the CW plant, using two automatic samplers, model Liquiport 2000 RPT20 (Endress + Hauser).

During the first campaign, carried out between January and December 2006, 1–2 paired inlet and outlet samples were collected weekly. A second campaign carried out between September 2008 and May 2010 consisted of the weekly collection of 3–5 paired inlet and outlet samples.

Physical and chemical analysis

Macro-parameters

Oxidation–reduction potential (ORP) and pH of wastewater and the suspension of particulate material into wastewater were measured using a portable meter, model 3310 (WTW, Weilheim, Germany) equipped with a temperature sensor and coupled with a SenTix® ORP electrode (WTW, Weilheim, Germany) equipped with a temperature sensor and with an LDO10110 sensor coupled with an integrated temperature sensor (accuracy ± 0.001 pH units, ±0.1 mV and ±0.1 °C).

The dissolved oxygen (DO) was measured in the inlet and outlet of the CW with a portable meter HQ40D (HACH Instruments, Loveland, CO, USA) equipped with an LDO10110 sensor coupled with an integrated temperature sensor (accuracy ± 0.1 mg O₂ L⁻¹ and ±0.1 °C).

Chemical parameters

Total chromium concentration in wastewater (water and suspended particulate material) was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer (Waltham, MA, USA) Optimal DV 2000, after acidic-oxidant digestion with Suprapur® grade reagents, using a microwave system ‘ETHOS-1’ (Milestone S.r.l., Bergamo, Italy) with pulsed-mode emission. In particular, 3.5 mL of HNO₃ 65% and 0.5 ml H₂O₂ 30% were added to 12.5 mL of inlet or outlet wastewater and digested using the following microwave temperature program: from room temperature to 120 °C in 2 min, isotherm at 120 °C for 3 min, from 120 to 190 °C in 5 min and finally, isotherm at 190 °C for 20 min. The resulting solutions were taken up to 25 ml with purified water before ICP-OES analysis. Quantification was performed by external standard calibration curves.

Hexavalent and trivalent chromium were determined according to the IRSA Italian Official Methods 3150-B2/B3 for water and wastewater analysis. Briefly, Cr(VI) forms a complex with APDC which is extracted by chloroform, whereas Cr(III) remains in the aqueous phase and can be directly determined after separation from the organic phase. The latter is treated with HNO₃ 5 mol/L in order to destroy the complex APDC-Cr(VI), and the aqueous-acidic phase is analyzed for Cr(VI) by ICP-OES.

Quality control samples

A quality control (QC) procedure for chromium analysis of water samples was performed by spiking 100 μL of a freshly prepared aqueous solution of K₂Cr₂O₇ and CrCl₃ both at a concentration of about 300 mg L⁻¹, in 500 mL of milli-Q water, thus obtaining a spiked solution of ~20 μg L⁻¹ in both Cr(VI) and Cr(III). The QC samples (n = 3) were analyzed for CrTOT, Cr(VI) and Cr(III) according to the methods described above and the recoveries achieved were found in the range of 95–98, 93–97 and 92–94%, respectively.

Blanks and limits of quantification

Blanks for CrTOT, Cr(VI) and Cr(III) analysis were performed following the same analytical procedures adopted for the sample analysis, without adding the matrix (wastewater).

The blank contributions were found in the range of 0.8–1.1 μg L⁻¹ for total and trivalent chromium, and 0.15–0.24 μg L⁻¹ for hexavalent chromium; therefore, the limits of quantification (LOQ) were considered equal to 2 μg L⁻¹ for CrTOT and Cr(III) and 0.5 μg L⁻¹ for Cr(VI). Since the method for the speciation of hexavalent chromium is more sensitive than the one for the trivalent form, chromium speciation in wastewater was carried out by analyzing Cr(VI).

Data analyses

Microsoft® Office Excel 2003 (Microsoft Corporation, Redmond, WA, USA) was used for the preparation of histograms. In order to evaluate the significance of the differences between mean values, the t-test and the non-parametric Dunnett T3 contrast test were carried out using the statistical package SPSS 13.0 (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

The mean values and ranges of selected physico-chemical parameters determined in the inlet and outlet of the h-SSF
The CW system during the two measurement campaigns are reported in Table 2. Inlet and outlet mean pH values were not statistically different, in accordance with the very low concentrations of inlet ammonium and nitrate and the resulting negligible occurrence of nitrification/denitrification processes (data not shown). Elevated inlet values were found for DO and ORP, probably due to the ozone treatment performed immediately before the wastewater entered the wetland. The ORP and DO values showed a statistically significant decrease from inlet to outlet, in accordance with the basically anaerobic characteristics of subsurface flow wetlands.

Throughout the entire investigation period, inlet concentrations (aqueous and particulate phases) were found in the range of 5.6–59.3 and 1.0–20.1 µg L\(^{-1}\), for total and hexavalent chromium respectively. Therefore, Cr\(_{\text{TOT}}\) concentrations found in the inlet were always much lower than the Italian legal limit for water reuse (100 µg L\(^{-1}\)). Conversely, hexavalent chromium concentrations in the influent were often higher than the maximum value permitted by the Italian regulation (5 µg L\(^{-1}\)), evidencing the necessity to treat wastewater before recycling it.

The variations of about one order of magnitude between the lowest and the highest value of inlet concentrations for both total and hexavalent chromium were the result of two main factors: (i) a significant decrease of production, due to economic reasons, registered in the industrial textile district of Prato during 2008 and thereafter, in respect to previous years, and ii) the Bacia cavallo ASP receives wastewater from an industrial district that does not operate on Saturdays and Sundays. In fact, when the mean inlet concentrations determined during the measurement campaign carried out in 2006 were compared to the ones for the period 2008–2010, a statistically significant difference (\(p < 0.001\)) was found for both Cr\(_{\text{TOT}}\) and Cr(VI) (see Figure 1). A statistically significant difference (\(p < 0.001\)) in both cases was also observed when data collected on working days were compared to those of the weekend, with the latter lower than the former (data not shown).

The percentage variation coefficients found for inlet hexavalent chromium (51.3 and 52.1% in 2006 and 2008–2010 campaigns, respectively) were much higher than the ones for Cr\(_{\text{TOT}}\) (35.0 and 39.5%) evidencing an additional source of variability for the former rather than for the latter. In particular, when Cr(VI) inlet concentrations regarding Saturdays and Sundays (days on which the ozone treatment was not operating) were compared to those determined from Tuesday to Thursday (days on which the ozone treatment was fully operating), it was evident that Cr(VI) was significantly more abundant in the presence of ozone treatment. In this case, in fact, the hexavalent form accounted for about 36% of total chromium, whereas without ozone it only represented about 20% of the total chromium concentration. These findings evidenced the role of ozone treatment in the destruction of the complexes between azo-dyes and Cr(III), and in the subsequent oxidation of the trivalent form into the hexavalent form; in this regard, in fact, it should be noted that the redox potential of Cr(VI)/Cr(III) at the pH values of the CW inlet (range: 6.32–8.03) is included between approximately 0.75 and 0.50 V (Beverskog & Puigdomenech 1997) and is therefore much lower than the corresponding value for O\(_3\)/O\(_2\) (2.07 V) (von Gunten 2003).

As regards the performance of the h-SSF CW, in both the investigated periods, chromium concentrations in the outlet were significantly lower than those found in the inlet (\(p < 0.001\) for both total and hexavalent chromium) evidencing that the CW is effective in the removal of the different forms of chromium. Effluent concentrations of Cr(VI) were included between values lower than the
quantification limit and 4.5 $\mu$g L$^{-1}$, and were therefore constantly lower than the Italian legal limit for water reuse. Thus it can be stated that the h-SSF CW successfully treated hexavalent chromium for water recycling when a HLR of 13.3 cm day$^{-1}$ was adopted. In this regard, it should be noted that this HLR value is two or three-fold higher than the ones commonly applied to subsurface horizontal CWs (Kropfela et al. 2009).

In 2006, mean removals of about 55 and 67% were obtained for total and hexavalent chromium, respectively. In the subsequent campaign, Cr$_{TOT}$ removal was about 40% and therefore lower than the one previously determined. Conversely, the removal of the hexavalent form was 71%, evidencing a slight increase compared to the results of 2006. Two considerations can be drawn from the results mentioned above: (i) the removal efficiency of trivalent and hexavalent forms of chromium behaved differently with the increase in age of the CW system, since the removal of Cr(VI) was constant while that of Cr(III) significantly decreased during the wetland operation; (ii) the wetland considerably changed the relative percentage of the hexavalent and trivalent forms, giving rise to an effluent that was much less toxic than the inlet wastewater in reference to the presence of Cr(VI).

The decrease of Cr(VI) along the CW system was a consequence of its reduction to the trivalent form that may occur under anoxic conditions and in the presence of an electron donor, such as bivalent iron and/or sulfides and/or reducing organic compounds. The resulting trivalent chromium can be stored in the reed bed, mainly through precipitation and/or complexation reactions with organic matter, as suggested by Makos & Hrncir (1993), but the importance of the different mechanisms in a field-scale CW still needs to be clarified. A direct uptake of chromium by Phragmites australis obviously cannot be ruled out, although current literature data indicate that the actual phytoextraction efficiency of this aquatic macrophyte is poor (Lesage et al. 2007a). However, a role of wetland plants in the reduction of Cr(VI) to Cr(III) through the release of root exudates containing readily oxidizing organic compounds has been suggested by Xu & Jaffé (2006) in a laboratory study.

**CONCLUSIONS**

This research evidenced the very good performance of the h-SSF CW in order to obtain an effective decrease of Cr(VI) concentrations in the effluent and to comply with the requirements of Italian regulations for water reuse. Based on the data obtained, it could be estimated that a full-scale system of about 3.5 ha would be capable of satisfying the demand for recycled water in the Prato textile industrial district.

The results of this study indicate that the removal of hexavalent chromium, which is based on its reduction to Cr(III), can be sustained in the long term. The decrease of trivalent chromium concentrations in the effluent, which is based on its storage in the reed bed, is more sensitive to the age of the CW system; thus, the treatment efficiency of trivalent chromium will become gradually lower, tending to reach zero with the increase in age of the CW.

Even though the mechanisms governing the reduction of the hexavalent chromium and the storage of the resulting trivalent form have not been completely clarified in CWs, this study has evidenced the advantage of the multiple processes by which wetlands transform and immobilize pollutants.

Further research should be devoted to the investigation of chromium removal mechanisms occurring in full-scale h-SSF CW, in order to better understand the processes involved in the reduction of the hexavalent form to the trivalent form, and in the storage of chromium in the reed bed. In addition, efforts should be made to assess how important the role of Phragmites australis is for chromium phytoextraction and phytostabilization, especially in the case of treatment of wastewater highly polluted with chromium. In fact, the studies currently reported in literature have focused on domestic wastewater with a very low input of chromium (Lesage et al. 2007a, b). Moreover, in these studies there has been a lack of a comprehensive control of parameters such as inlet concentrations and/or flow rate, the knowledge of which is of fundamental importance for accurately calculating a mass balance of pollutants.

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