Effect of operational parameters on the performance of a horizontal subsurface flow constructed wetland treating secondary cheese whey and Cr(VI) wastewater

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Abstract—While constructed wetlands have proved to be successful in the treatment of various wastewaters, their ability to co-treat wastewaters with different characteristics has not been thoroughly examined. To this end, four pilot-scale horizontal subsurface flow constructed wetlands were used to co-treat secondary cheese whey and hexavalent chromium. Based on the experimental results constructed wetlands proved to be effective in co-treating these two wastewaters as they achieved 100% removal of hexavalent chromium, while mean COD removal ranged between ranged between 50% and 70%.

Keywords—constructed wetlands, horizontal subsurface flow, vegetation, hexavalent chromium, secondary cheese whey

I. Introduction

Constructed wetlands (CWs) have been used to treat not only municipal wastewater but also wastewaters containing high pollutant loads (e.g. agro-industrial wastewaters) or toxic substances (e.g. hexavalent chromium - Cr(VI)) (Schaafsma et al., 2000; Dotro et al., 2012; Stefanakis et al., 2014). Horizontal subsurface (HSF) CWs treating secondary cheese whey (SCHW) or Cr(VI) have been identified as more effective than other CW types (Michailides et al., 2013; Sultana et al., 2014a;b). Although the ability of CWs to treat various wastewaters and adapt to fluctuating pollutant loads has been proved, their ability to co-treat wastewaters with different characteristics has not been thoroughly examined. This study aims to examine the ability of HSF CWs to co-treat SCHW and Cr(VI). For this reason, four pilot-scale HSF CWs, which had previously treated either SCHW or Cr(VI), were tested (Sultana et al., 2014a;b).

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п. Materials and Methods

A. Pilot-scale CW units

The four pilot-scale HSF CWs were trapezoidal tanks with dimensions 1.26 m long, 0.68 m wide (upper base), 0.73 m deep, and a total volume of 0.62 m³. The units were filled with fine gravel (D50=6mm). Two of the pilot-scale HSF CWs had been previously used (1st operational period) to treat SCHW and. One was planted (SCHW-P) with common reeds (Phragmites australis) and the other was kept unplanted (SCHW-U). The other two pilot-scale units HSF CWs had been used previously (1st operational period) to treat Cr(VI) and, again, one was planted (Cr-P) with common reeds (Phragmites australis) and the other was kept unplanted (Cr-U). During the 2^{nd} operational period, tap water enriched with Cr(VI) and SCHW was introduced into the four CW units. HRTs and influent concentrations of chemical oxygen demand (COD) and Cr(VI) were similar to those used in our previous experimental works (Sultana et al., 2014a;b). Thus, two HRTs were applied (i.e. 4 and 8 days), while influent COD concentrations ranged from 1300 to 4100 mg/L for the SCHW-P and SCHW-U units, and from 1800 to 4000 mg/L for Cr-P and Cr-U units. In addition, Cr(VI) influent concentrations ranged from 0.4 to 5 mg/L for SCHW-P and SCHW-U and from 2.2 to 5.5 mg/L for Cr-P and Cr-U. The four pilot-scale units operated co-treating SCHW and Cr(VI) for seven months (April to October 2013). Evapotranspiration (ET) was assessed on a daily basis. Precipitation levels and influent and effluent volumes were measured daily. During days with high solar radiation and temperatures, ET exceeded the wastewater influent volumes, leading to a reduction in the units' water level, as ET values reached 15.5 L/d.

B. Water quality monitoring

Water samples were collected with a frequency equal to the HRT, from the influent and the effluent points of each unit. In the laboratory, the water samples were analyzed for Cr(VI) following the 3500-Cr D Colorimetric method with a detection limit of 0.013 mg/L (APHA, 1998). COD was monitored by the absorbance of the sample after dichromate digestion at 150 °C for 2 h in the presence of silver and mercury sulfates (closed reflux method, APHA et al., 1989). The absorbances



were measured using a HANNA C99 Multiparameter Bench Photometer (digested in a HANNA instruments C9800 REACTOR). Meteorological data were obtained from the nearest meteorological station (in Agrinio city). For the sixmonth operation period, mean temperature was 23.5°C and total precipitation was 286 mm.

III. Results and discussion

A. Cr(VI) and COD removal

Figures 1 - 8 present time series charts for Cr(VI) and COD influent and effluent concentrations for all pilot-scale CW units. SCHW-U and SCHW-P did not show any difference in Cr(VI) removal as the average removal rate was 100% (Figs. 1 and 2). It should be mentioned that during the 1st operational period, these two pilot-scale units treated only diluted SCHW. Therefore they showed great adaptability when co-treating the cheese whey and Cr(VI). Similar behavior was also shown by the other two pilot units (Cr-P and Cr-U) in removing Cr(VI), where the average removal rate was 100% for both units (Figs. 3 and 4).



Figure 1. Time series chart of Cr(VI) influent and effluent concentrations in SCHW-U.



Figure 2. Time series chart of Cr(VI) influent and effluent concentrations in SCHW-P.



Figure 3. Time series chart of Cr(VI) influent and effluent concentrations in Cr-U.



Figure 4. Time series chart of Cr(VI) influent and effluent concentrations in Cr-P.

The average COD removal efficiency was 70.7% for the SCHW-P and 48.27% for the SCHW-U unit (Figs. 5 and 6). SCHW-P showed over 50% removal rate for COD, when the influent COD concentration ranged between 2000 mg/L and 5000 mg/L for both HRTs (8 and 4 days). During the 1st operational period both SCHW-P and SCHW-U, ,presented slightly higher COD removal rates (74.8% for the SCHW-P and 51.5% for the SCHW-U). These differences in COD removal could be attributed to the possible toxic effects of Cr(VI) on the microorganisms that remove organic matter. Cr-P and Cr-U's mean COD removal efficiency was 65.6% and 58.2%, respectively (Figs. 7 and 8). Cr-P and SCHW-U.





Figure 5. Time series chart of COD influent and effluent concentrations in SCHW-U.



Figure 6. Time series chart of COD influent and effluent concentrations in SCHW-P.

B. Effect of vegetation

Although unplanted (SCHW-U and Cr-U) and planted (SCHW-P and Cr-P) units recorded the same Cr(VI) removal rates (100%), the presence of vegetation in CWs is crucial for the treatment of Cr(VI) because it can slow down the flow rates in the wetland so that metals have more time to be absorbed and precipitated from the plant biomass (Sultana et al., 2014a). SCHW was selected because of its high nutritional value as it contains lactose, proteins, calcium, nitrogen and phosphorus (Prazeres et al., 2012). Therefore, using the mixed wastewater combination of SCHW and Cr(VI) solution, the reed plants grew rapidly and microorganism activity increased.



Figure 7. Time series chart of COD influent and effluent concentrations in Cr-U



Figure 8. Time series chart of COD influent and effluent concentrations in Cr-P.

The effect of the plants on COD removal rate was also analyzed using the Paired t-test of SPSS. The 95% confidence levels for the SCHW-P and SCHW-U units were between 11 and 0.8, while for the Cr-P and Cr-U units the values were between 16 and 1.2. Therefore, the presence of plants significantly favoured the removal of organic matter, although the main mechanism for the removal of organic matter is the activity of aerobic and anaerobic bacteria (Stefanakis et al., 2014). The highest removal efficiency of the planted unit may be due to enhanced oxygen supply in the CW's porous media provided by the plant roots.

c. Comparison with the 1st operational period

To compare the removal rates of Cr(VI) and COD during the two experimental periods, specific time periods were selected during which average temperature (approximately



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 20° C) did not show significant differences (p = 0.229> 0.05), and HRTs (4 days) and influent concentrations of Cr(VI) (approximately 5%) and COD (approximately 2550 mg/L) were constant. One-way ANOVA analysis was performed for the Cr-P and Cr-U units to investigate whether the removal efficiencies of Cr(VI) showed statistically significant differences between the two operational periods. Results showed that the removal rate of Cr(VI) between the two operational periods was statistically significant (p = 0.000<0.05) in the Cr-P. This difference may be because the first operational period was the initial operating period (first 90 days). Usually during these early days of treatment, CW performance is not stable. After the first adaptation stage, Cr-P consistently showed 100% removal efficiency of Cr(VI). On the other hand, the Cr-U also showed statistically significant differences in removal of Cr(VI) between the two sessions (p = 0.000 < 0.05). This fact enhances the view that the main removal mechanism of Cr(VI) during the 2nd operational period in the Cr-U unit was the microbial activity and not adsorption to plant biomass. From the above it can be concluded that SCHW could be used as a carbon source for the microorganisms that reduce Cr(VI).

One-way ANOVA statistical analysis was also performed for SCHW-P and SCHW-U, to investigate whether removal efficiencies of COD in the two pilot units show statistically significant differences between the two operational periods. The ANOVA results showed that the removal of COD between the two periods did not show statistically significant differences (p=0.576> 0.05) for the SCHW-P unit. Similarly, SCHW-U also did not show any statistical significant differences in COD removal between the two periods (P = 0.976> 0.05). Therefore, Cr(VI) showed no toxic effects likely to inhibit the biological degradation of organic matter.

I. Conclusions

CWs are effective not only in treating SCHW and Cr(VI) separately but also as a combined wastewater. Pilot-scale CWs showed an ability to adapt to different wastewater types as they showed Cr(VI) removal rates of up to 100%, while COD removal rates were also significant (around 70%). Vegetation has a positive effect on COD removal, while the main removal mechanism of Cr(VI) appears to be microbial activity.

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