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"Constructed wetlands for the reuse of industrial wastewater: a case-study"

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Abstract

The use of phytoremediation systems to enhance the treatment of industrial wastewater coming from a standard depuration process in order to allow their reuse can potentially lead to several interesting benefits (costs savings for depuration processes, freshwater and energy supply with a consequent reduction of the overall environmental impact of the industrial sites). In this work the case study of a large automotive plant (FCA plant in Verrone, Piedmont, NW Italy) was analysed, with the aim of evaluating the possible application of a phytoremediation system (constructed wetland, CW) to treat the effluents of its existing wastewater treatment plant (WWTP, currently discharged into a watercourse) and reuse them in the industrial processes. For this purpose, a pilot CW system was set up with two different configurations horizontal and vertical. Experiments were carried out to identify the one characterized by the best abatement rate of the pollutant concentrations of the plant effluents. Results showed that the horizontal submerged flow system (HF) was the most efficient phytoremediation system suitable for the aging of the effluents of the existing WWTP in view of their possible reuse in the industrial processes. Furthermore, costs related to its scaling-up for a real application demonstrated that the CW can be the cheaper option compared to a traditional treatment process for wastewater reuse. The amount of treated water which may be reused can range from 55% to 80% of the effluents

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from the existing WWTP, with a consequent reduction of more than 80% in the current water supply from aquifers.

Keywords: industrial wastewater reuse, constructed wetlands, pilot phytoremediation treatment system, phytoremediation

1. INTRODUCTION

Industrial wastewater reuse can lead to several environmental improvements since it decreases discharge of pollutants and abstraction of high-quality water from ground and surface aquifers (Mohsen and Jaber, 2003), and also allows energy recovery and industrial processes optimization (Bixio et al., 2006). The use of phytoremediation to enhance the treatment of industrial wastewater coming from a standard depuration process with the aim of allowing its industrial reuse, is a new concept of a well-known technology that can be applied to several types of wastewater flows. Constructed wetland (CW) systems are used worldwide for removing pollutants from several types of wastewater. Their construction is relatively simple and their operational and maintenance costs are lower than conventional wastewater treatment technologies (DiMuro et al, 2014). The most used phytoremediation technology is the horizontal submerged flow system (HF), where the water level is slightly below the surface and the environment inside the beds is predominantly anaerobic. A well-defined oxygenated micro zone is developed around the rhizomes of the eleophytes, which determines the development of the aerobic bacterial film. The alternation of aerobic and anaerobic areas involves the development of several specialized microorganism families and the almost total disappearance of pathogens, particularly sensitive to rapid changes in the dissolved oxygen content. Organic matter, passing through the macrophytic rhizosphere, is decomposed by microbial action. Nitrogenous substances are also subject to nitrification and denitrification processes. Nitrification is strongly limited by oxygen shortage and reduced hydraulic retention time, while denitrification is predominant in anaerobic areas. Phosphorus and heavy metals are fixed for adsorption on the filling material and absorbed by the plants. The feeding of the beds is continuous and must be such as to allow uniform distribution of the entire bed width. A second type of phytoremediation technology is often used in the treatment of several types of wastewater it is called vertical submerged flow system (VS). Compared to the horizontal flow system, in the vertical flow ones the flow to be treated is slid

vertically through the fill medium. The inflow is provided in an intermittent manner (with load periods following the pause periods) by means of submerged pumps or siphon systems, when the gradients allow the entry of the fluids in the basin by gravity. The intermittent supply makes possible a high oxygenation of the medium. In fact, the liquid distributed throughout the surface gradually flows through the bottom of the tanks and the progressive emptying allows the air to infiltrate the interstices of the fill medium. Following intermittence, deeper layers alternate periods of oxidizing conditions at periods of reducing conditions and there is a constant replacement of the gases present in the soil. The principles on which the contaminants are removed are the same as those of the HF systems, but in the VF ones the environment is more oxygenated, allowing higher oxidation and degradation of the organic substance and nitrification processes. Although the benefits of constructed wetlands, in various configurations, have been proven for the treatment of domestic wastewater (Vymazal, 2005), combined sewer overflow (Ávila et al., 2013), refinery effluent (Kadlec and Wallace, 2008) and industrial and agricultural wastewater (Vymazal, 2014), further studies reporting their performance for the reuse of industrial wastewater are still lacking. Nowadays phytoremediation systems can be designed to work in situations that are quite far from their usual range of application, but their implementation for industrial wastewater reuse still needs to be adequately investigated (Wu et al., 2015), considering that it can lead to costs savings for depuration processes, freshwater supply, and energy consumption and to a consequent reduction of the overall environmental impact of industrial sites.

Furthermore, there is no literature on comparative studies between traditional technologies and constructed wetland systems aimed at water reuse. This research evaluates the possible implementation of a phytoremediation process for reusing for industrial purposes the effluents of the WWTP of a large automotive plant producing transmission gear for cars (Fiat Chrysler

Automotive plant in Verrone, Piedmont, NW Italy). The site is ISO 14001 certified and uses the World Class Manufacturing (WCM) method to improve its global efficiency with strong cost reduction. In order to reach the WCM gold medal the plant management decided to improve its water management system activating a water reuse policy. Water consumption and releases to water are among the main environmental aspects for which ISO 14001 certified plants of the automotive sector are committed towards improvement (Comoglio and Botta, 2012) and this strategy can lead to higher efficiency under both economic and environmental point of view in relation to a resource, water, which is progressively becoming more and more precious. The plant daily water supply (about 750 m^3/d) is satisfied by means of a group of pumping wells, while the plant sewer system collects civil wastewaters and effluents coming from industrial processes and transfers them to the WWTP as shown in Figure 1. The main aim of this research is to evaluate if a phytoremediation system (submerged vertical or horizontal) can be implemented as a final section of the existing WWTP for the enhancement of the effluents quality and their consequent reuse in the industrial processes to avoid/reduce the supply of groundwater from wells. For this purpose, specific experimental tests were carried out in a pilot phytoremediation treatment system, where the efficiency of two different constructed wetland systems for the treatment of the Verrone WWTP effluents were tested. Based on the experimental results, the most efficient phytoremediation system that could be adopted to allow the reuse for industrial purposes of the WWTP effluents was then compared from a technical and economical point of view with a traditional system, to evaluate if this innovative approach can be considered a feasible option or not.

Figure 1a

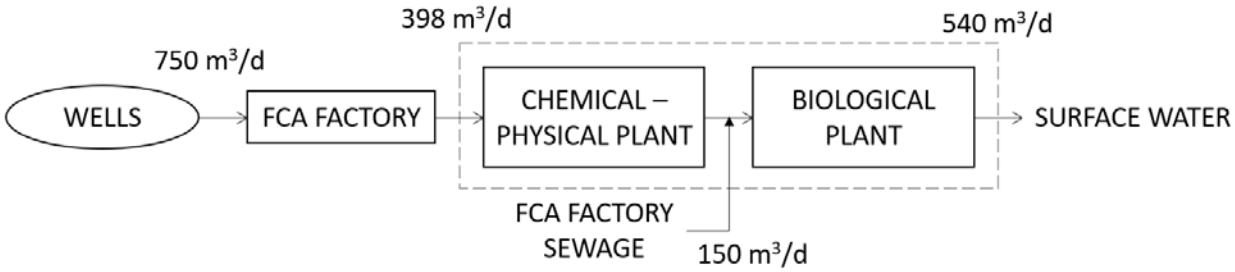


Figure 1b

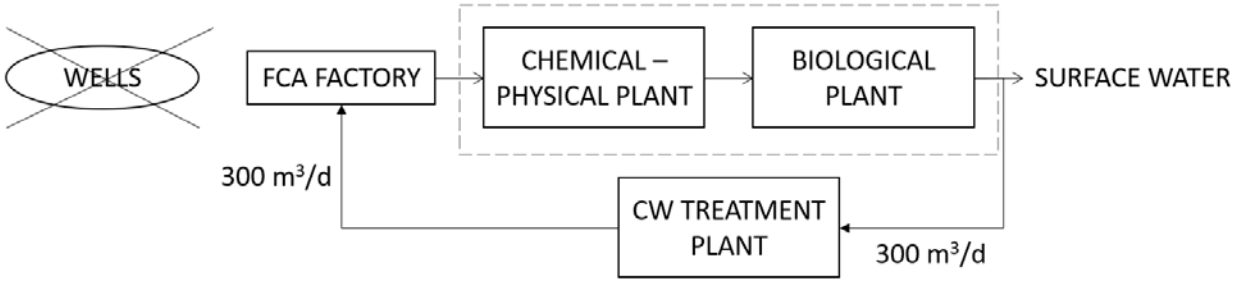


Figure 1 Graphical representation of the two plant layouts for industrial water cycle.

a Current industrial water cycle.

b Hypothetical scenario.

2. MATERIAL AND METHODS

2.1 Verrone plant industrial water supply

The Verrone plant water network is supplied by six wells (mean daily volume supplied: 750 m^3/d) located within the plant boundaries. Water for industrial uses is pumped and accumulated inside a buffer tank (20,000 m^3) which feeds the distribution network without any treatment. The mean chemical-physical characteristics of the industrial water are reported in Table 1, outlining electrical conductivity (EC) and salinity values which allow water to be considered as drinkable according to EC laws. Furthermore, chemical oxygen demand (COD), ammonia ($N\text{-}NH_4^+$), nitrous ($N\text{-}NO_2^-$) and nitric nitrogen ($N\text{-}NO_3^-$), and bacteria concentrations are low.

Table 1 Mean values of the flow rates and pollutants concentrations of wells water, existing wastewater treatment plant sections and final outlet.

Parameters	Wells water	Chemical – physical section inlet	Biological section inlet	Biological section outlet
Flow-rate (m^3/d)	750	398	540	540
pH	7.98	6.02	8.54	7.88
COD (mg/L O_2)	<1	810	480	61.3
Conductivity (µS/cm)	117			412
Suspended solids (mg/L)				20.5
Ammonia (mg/L)	<0.05		16.7	8.2
Nitrate (mg/L)	5.5			
Nitrite (mg/L)	< 0.025			
Nitric (mg/L)			0.18	16.3
Nitrous (mg/L)		<0.6	2.90	0.52
Iron (mg/L)	< 20 (µg/L)	0.44	0.53	0.42
Manganese (µg/L)	11.4	<0.1	<0.1	<0.1
P-total (mg/L)	<0.5	<0.5	1.84	1.67
Sulfates (mg/L)	3.80	5.48	3.46	16.3
Chlorides (mg/L)	4.30	63.7	37.1	52.4
Total surfactants (mg/L)	<1	10.2	4.90	1.62
Hydrocarbons (mg/L)	<1	25.5	10.1	4.80
Bacteria (UFC/100 ml)	<1			260

2.2 The existing WWTP

The sewage coming from industrial and civil buildings and technological waters originated inside the Verrone premises are processed at a WWTP located inside the factory property, made up of two treatment sections, a chemical-physical and a biological one. The chemical-physical section, where the technological effluents are preliminarily treated, is composed of: storage tank, API type oil separator, bath acidification, bath alkalinization, flocculation tank, a clarifier with a rotating bridge, neutralization tank and finally storage/balancing tank. The biological section is composed of: Venturi's flowmeter channel with data logging, automatic sand separation, nitrification-denitrification reservoirs, oxidation (active sludge treatment), activated sludge recirculation system, overflow fat tank collector, clarifier with rotating bridge, overflow tank and final discharge. The biological section receives the effluents that directly come from the sewage

network (150 m^3/d) and the technological effluents after their passage through the chemical-physical plant (398 m^3/d) as highlighted in Figure 1.

Table 1 shows the mean concentration values of the main water quality parameters measured at the inlet of the chemical-physical and biological sections, together with those measured at the final outlet of the WWTP. These last concentration values are rather low, indicating that the overall WWTP efficiency is good. However, comparing the quality of the water supplied from the wells with the one of the treated wastewater, it is evident that salinity is higher in the wastewater and therefore, N-nitric, sulfates and chlorides concentrations in the outlet must be reduced before a potential reuse in the factory.

2.3 Description of the pilot phytoremediation treatment system

The outdoor pilot treatment plant of the Department of Environmental, Land, and Infrastructure Engineering of Politecnico di Torino (Italy) was used to investigate the best setup to be applied to the case study. The system was initially developed to treat grey water (Comino et al, 2013a) and anaerobic digestion effluents (Comino et al., 2013b). Three constructed wetlands (CW) tanks were set to work with parallel configuration (Figure 2). After a commissioning period of vegetation stabilization and a gradual start-up of the system, the pilot phytoremediation treatment system was controlled periodically for three months (April to June). Treated water (effluents from the WWTP) transported from the Verrone plant was periodically supplied to the system inside a 1 m^3 polyethylene tank (inlet tank), continuously stirred to avoid settling of solids and completely integrated into the experimental pilot plant. Subsequently, electric pumps distributed the water into 3 parallel tanks characterized by different constructed wetland configurations. These were two vertical submerged flow (VF) beds that worked alternately, indicated as Vertical Flow A (VFA) and Vertical Flow B (VFB), and one horizontal submerged flow (HF) bed. Figure 2 shows the experimental plant layout.

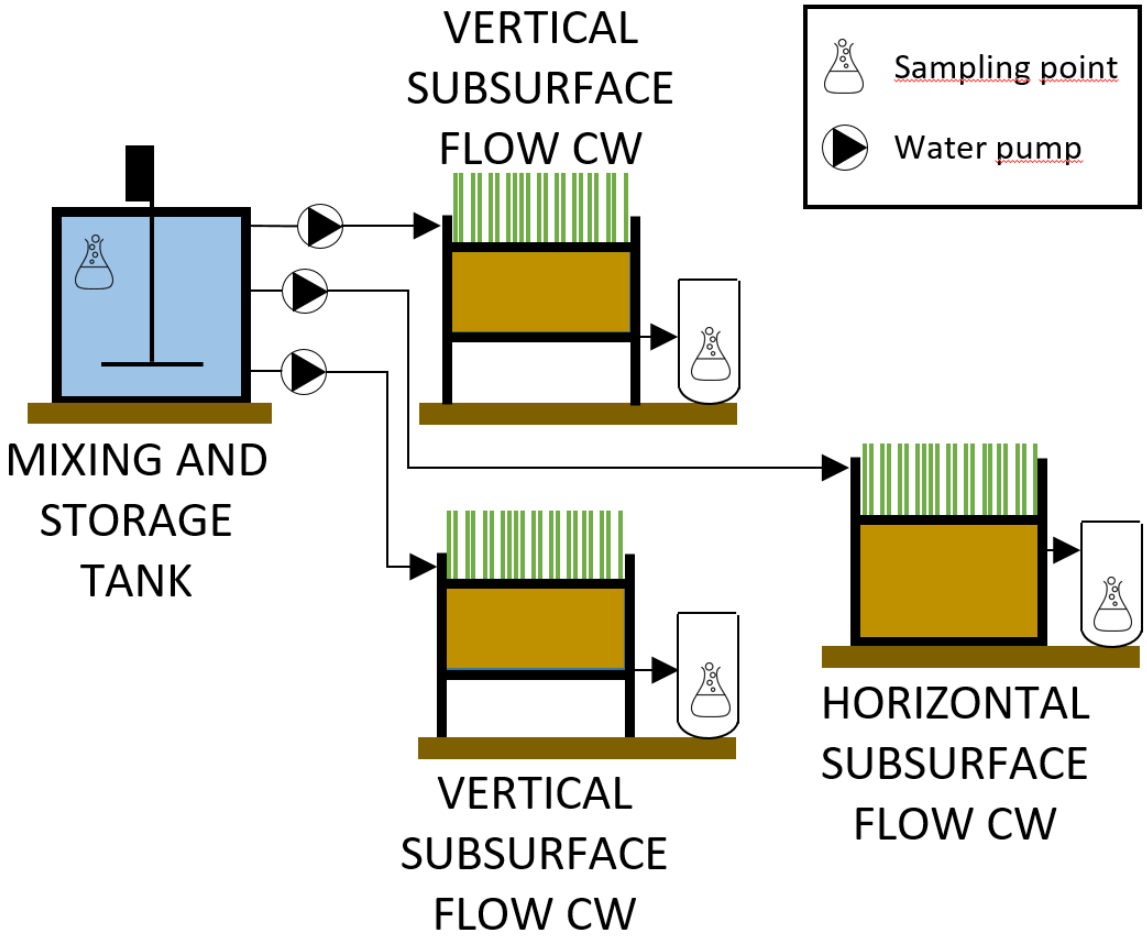


Figure 2 Layout of the CW pilot phytoremediation treatment plant used for the experiments.

The two VF wetlands had a surface area of about 1 m^2 each and operated alternatively in daily cycles. The intervals between the stop and go phase of the pumps were set based on past experiences in a range between 2 to 6 per day for each VF (Sigmund, 2006). This alternation of feed and rest phases was chosen due to several benefits for the system: controlling the growth of the attached biomass, maintaining aerobic conditions within the filter bed and mineralizing the organic deposits accumulated on the bed surface (Molle et al., 2008). The VF tanks were intermittently fed from the inlet tank by means of hydraulic pulses in a way to improve oxygen renewal. Two pumps worked alternatively, depending on the active cycle, to feed each of the VF beds. Each pump was ruled by a pre-configured timer, which was programmed to provide the

quantity of inlet water (50 L d^{-1}) defined as the optimal flow rate during the design of the pilot plant (Comino et al, 2013a). The water distribution was assured by a polyethylene pipe placed on the surface of the beds. Moreover, each VF tank was equipped with a passive aeration system linked from one side with the discharge system, placed on the bottom of the tank, and on the other side with the atmosphere on the tank surface. The continuous feeding of the HF wetland was performed using an electric pump that moved water inside a Mariotte's bottle configured to allow a constant flow of 50 L d^{-1}. Both effluents of the VF – with regard of the one in operation - and HF beds were accumulated into a 100 L tank, where the sampling and the monitoring of the effluents were carried out. The experimental setup allowed to process the effluent stored inside the storage tank, checked every day to ensure a fresh sample, almost once per week. All the CWs were constructed using HDPE steel wire protected tank and were planted as follow: one VF tank with *Juncus maritimus Lam* (sea rush) and one with *Typha latifolia* while the HF was planted with *Cyperus papyrus* (papyrus sedge). Vegetation was well established in all the constructed wetlands. The treatment plant was set to work under a constant flow of approximately 50 L d^{-1} during the whole experimental period, giving an average hydraulic loading rate (HLR) and organic loading rate (OLR) of 5 cm d^{-1} and 0.9 g COD $m^{-2}d^{-1}$ (Table 2).

Table 2 Main characteristics of the constructed wetland systems.

Parameter	Unit	Value
Geo. Position	-	45°03'48.76"N 7°39'39.61"E
Height	m a.s.l.	249
Wastewater		Industrial treated wastewater
Load	BOD_5 (mg/L)	18
Inflow	L/d	50
Surface VF	m^2	1.98
Surface area HF	m^2	0.99
VF filling media	Depth of layers: cm	Top 10 cm, coarse material
	Grain size Ø: mm	Middle 30 cm, sand Ø 1-2 mm
		Bottom 10 cm, gravel Ø 3-8 mm
VF depth	m	0.5
HF filling media	Depth of layers: cm	Entirely filled with gravel Ø 3-8 mm
	Grain size Ø: mm	
HF depth	m	0. 5
HLR – VF	cm/d	2.53
HLR – HF	cm/d	5
HRT – HF	D	4
OLR	$gCOD/m^2/d$	0.9
Primary treatment	-	Not present
Operating since	-	September 2009

2.3 Sampling strategy

Since one of the purposes of this study was to assess the overall treatment performance of the pilot system to evaluate if phytoremediation can handle treated industrial wastewater to enhance their characteristics for reuse, the pilot phytoremediation treatment system was monitored daily for three months. Furthermore, at the arrival of the Verrone plant WWTP effluents, a sample was collected and analyzed in the laboratory. Other samples were taken at the outlet of each treatment tank after a 5 days period, to consider all hydraulic retention times (HRT). The effluent of both VF tanks was sampled at the subsequent storage tank, just after a feeding pulse to the VF bed, to ensure a fresh sample (Figure 2). The following parameters were analyzed in the laboratory: chemical oxygen demand (COD), total suspended solids (TSS), pH, electric conductivity (EC 20°C), alkalinity, ammonium, nitrate, sulfate, chloride, sodium, potassium, calcium, magnesium, aluminum, iron, and zinc.

2.4 Analytical methods

Daily onsite measurements of water temperature, DO, pH, and EC were performed by using a multiparameter Hanna Instrument 9828.

Conventional industrial wastewater quality parameters, including TSS, alkalinity, ammonium (NH_4^+), nitrate (NO_3^-), sulphate ($SO_4^=$), chloride (Cl^-), COD and metals (Na, K, Ca, Mg, Fe, Al, Zn) were determined by using Standard Methods (APHA, AWWA, WEF, 2005).

The TSS analysis was performed by filtration of a known volume of sample on a membrane of cellulose acetate with a degree of retention 0.45 microns. Alkalinity was performed within 24 hours from the delivery/collection of the sample by automatic titration (SI Analytics WA 50 ml titrator) of a 50 ml sample with a 0.1 N HCl solution.

Ammonium and nitrate were measured on samples previously filtered at 0.45 µm using a spectrophotometric determination with Macherey-Nagel test kits, Kit Ammonium Nanocolor, 1-05 and Kit Nitrate Z Nanocolor, 1-63, respectively.

Sulfate was determined as barium sulfate by a turbidimetric determination: sulfate reacts with barium chloride to give barium sulfate (insoluble) held in suspension by glycerine. It was detected at the wavelength of 420 nm.

The analysis of chloride was performed by a spectrophotometric determination at 463 nm in the presence of ferric alum and mercuric thiocyanate.

The analysis of COD was performed by oxidizing oxidable substances with a 0.12 N potassium dichromate solution for 2 hours at 150°C in the presence of concentrated sulphuric acid. The unreacted oxidant was finally titrated with a 0.0625 N iron and ammonium sulfate solution.

Metals were determined by using an ICP-OES (Optima 2000DV, Perkin Elmer) after samples filtration (0.45 µm) and acidification. The analytical methods with the employed equipment and detection limits are resumed in Table 3.

Table 3: specifications of equipments and detection limits of adopted analytical methods.

Parameter	Equipment	Detection Limit
TSS	Analytical balance	0.0001 g
Alkalinity	Automatic titrator	0.1 mg/L (no dilution)
NH_4^+	UV-Vis spectrophotometer	0.01 mg/L (no dilution)
NO_3^-	UV-Vis spectrophotometer	0.01 mg/L (no dilution)
Cl-	UV-Vis spectrophotometer	0.01 mg/L (no dilution)
$SO_4^=$	UV-Vis spectrophotometer	0.01 mg/L (no dilution)
COD	Digestion / manual titration	2 mg/l (no dilution)
Na	ICP-OES – axial view, λ = 589.592 nm	0.00690 mg/L
K	ICP-OES – axial view, λ = 766.490 nm	0.01 mg/L
Ca	ICP-OES – radial view, λ = 393.366 nm	0.0002 mg/L
Mg	ICP-OES – axial view, λ = 285.213 nm	0.00016 mg/L
Al	ICP-OES – axial view, λ = 396.153 nm	0.00280 mg/L
Fe	ICP-OES – axial view, λ = 238.204 nm	0.00046 mg/L
Zn	ICP-OES – axial view, λ = 213.857 nm	0.00018 mg/L

Furthermore, since the pilot plant was built to process inlet wastewater with pollutant concentrations higher than the current one, a leaching test was performed to verify the influence of CWs substrate on the outlet wastewater quality. The test was carried out following the UNI 10802 procedure. The bed portion was predominantly made up of gravel size between a few millimeters and a few centimeters. It was used a solid - liquid relationship equal to 1:10, a 24-hour contact time, agitation 50 rpm. Analyses were performed on passing fraction at 0.45 microns. The gravel sample was quartered to obtain 4 equivalent mass rates. Two aliquots were put in contact with deionized water, the remaining two aliquots were put in contact with the effluent that fed the system of constructed wetlands.

Unless otherwise stated, all data are expressed as a mean ± standard error. When possible the mean values of all the parameters were examined for significance by single factor Analysis of Variance (ANOVA) using the software JMP version 9 (SAS Institute Inc, Cary, North Carolina, USA). When F values showed significance, individual means were compared using Tukey's honest significant difference at $P \leq 0.01$.

3. RESULTS AND DISCUSSION

3.1 Performance of the pilot phytoremediation treatment system

Average values, standard errors, and comparison between averages of water quality parameters for every CW tank are shown in Table 3. As already noticed by Avila et al. (2013) the input wastewater arrived oxygenated (5.73±0.15 mg O_2 L^{-1}) inside the CWs system since, in its transport from the WWTP to the inlet tank, it was pumped several times and then continuously stirred. The high value of redox status confirmed this behavior (+209.9±15.6 mV). The DO concentration remained almost the same inside the two VF beds (5.47±0.15 and 5.48±0.15 mg O_2 L^{-1}) where water percolation through the substrate and around root zone was oxidized. On the contrary, when the inlet wastewater passed through the HF bed, where the longer hydraulic retention time and deep substrate zones contributed to creating anaerobic and anoxic zones, the DO and ORP values significantly decreased (1.98±0.15 mg O_2 L^{-1} and +90.4±15.6 mV).

As shown in Table 3 the pollutants concentration values of the inlet water (effluents of the Verrone WWTP) were already low, and compatible with the Italian law for their discharge into surface waterbodies, but they had to be further reduced to allow their industrial reuse (Table 4). In Figure 3 the main water parameters removal percentage for each tank (inlet wastewater vs effluent from each tank, VFA, VFB and HF) are shown. With regards to COD, since the concentration values of the incoming water were low and similar to the usual concentration values set for the effluents of a CW system (18±2 mg L^{-1}) (Metcalf and Eddy, 1991), it was not so obvious to obtain additional removals. However positive elimination rates were obtained for the VF beds (around 20%) while significantly higher values were recorded at the HF tank (60 %). Vymazal (2005) indicated VF technology as more efficient, since this type of systems allows a high oxygen transfer rate, which positively contributes to the removal efficiency of organic matter as reported by Gross et al. (2007). In this case, where the incoming concentration values were very low, the higher retention time typical of HF systems resulted in a better removal performance.

Furthermore, one of the most interesting aspects of the VF systems, consisting in managing high organic and hydraulic loading rates without risk of granular media clogging as reported by Weedon (2003) in a two-year study conducted on a compact vertical flow bed and by Molle et al. (2006), that investigated the hydraulic limits of reed beds.

Table 4 Analytical data for water quality parameters in the different tanks of the pilot plant treatment system[a], the inlet represents the main characteristic of the wastewater coming from the WWTP.

	pH	T (°C)	DO (mg/L)	ORP (mV)	EC (µS/cm)	COD (mg/L)	Alkalinity (mg/L)	TSS (mg/L)	NH_4+ (mg/L)	NO_3- (mg/L)
Inlet	7.47 ±0.03(b)	19.78±0.54(A)	5.73±0.15(a)	209.9±15.6(A)	255.00 ±5.14(c)	18±2(A)	80.2±2.5(d)	1.36±0.28(A)	0.11±0.01(a)	18.9±1.0(A)
VFA	7.49±0.02(b)	19.19±0.54(A)	5.47±0.15(ab)	205.4±15.6 (A)	331.89±3.83(a)	15±1(A)	123.5±1.9(b)	0.22±0.21(B)	0.01±0.01(b)	17.9±0.8(A)
VFB	7.77±0.02(a)	19.19±0.54(A)	5.48±0.15(ab)	205.4±15.6(A)	285.44±3.83(b)	14±1(AB)	93.3±1.9(c)	0.01±0.21(B)	0.01±0.01(b)	17.6±0.8(A)
HSF	7.82±0.02(a)	20.37±0.54(A)	1.98±0.15(b)	90.4±15.6(B)	331.56±3.83(a)	7±1(B)	145.8±1.9(a)	0.01±0.21(B)	0.01±0.01(b)	3.48±0.76(B)
	Cl^- (mg/L)	$SO_4^=$ (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Zn (µg/L)	Fe (µg/L)	Al (µg/L)	
Inlet	21.8±1.08(a)	6.84±0.23(AB)	6.14±0.35(a)	2.01±0.15(A)	23.51±0.70(c)	9.37±0.16(A)	418±13(a)	348.09±25.476(A)	48.0±55.2(a)	
VFA	18.32±0.8(ab)	7.57±0.17(A)	4.89±0.26(a)	1.67±0.11(A)	51.8±0.52(a)	5.28±0.12(C)	64.1±9.5(c)	13.5±19.0(B)	31.9±41.1(a)	
VFB	19.7±0.8(a)	6.97±0.17(AB)	5.08±0.26(a)	1.9±0.11(A)	42.5±0.52(b)	5.04±0.12(C)	112±10(b)	24.9±19.0(A)	192±41(a)	
HSF	15.41±0.8(b)	6.33±0.17(B)	5.68±0.26(a)	0.39±0.11(B)	52.6±0.52(a)	6.69±0.12(B)	87.3±9.5(bc)	6.53±18.98(A)	41.0±41.1(a)	

[a]Within each column, values followed by different capital (A), (B) and (C) letters, and values followed by different lower case (a), (b), (c) and (d) letters are significantly different at P ≤ 0.01 level.

Table 5 Comparison among the EPA water quality standards for industrial reuse and related values at the pilot phytoremediation treatment plant inlet, WWTP outlet, and at the three CWs systems outlets.

	EPA standard for Industrial reuse		Inlet	VFA Outlet	VFB Outlet	HSF Outlet
pH	--	7.0-8.0	7.47	7.49	7.78	7.82
EC	µS/cm	150-200	**255**	**332**	**285**	**332**
Alkalinity	ppm $CaCO_3$	40-60	**80.2**	**123**	**93.3**	**146**
NO_3^-	ppm NO_3^-	5-10	**18.9**	**17.9**	**17.6**	3.48
Cl-	ppm Cl-	5-15	**21.8**	18.3	19.6	15.4
$SO_4^=$	ppm $SO_4^=$	4-8	6.84	7.57	6.97	6.33
Ca	ppm Ca	20-30	23.5	**51.8**	**42.5**	**52.6**
Mg	ppm Mg	5-10	9.38	5.28	5.04	6.69
Na	ppm Na	10-15	**6.14**	6.02	6.32	6.84
K	ppm K	1-3	**2.01**	1.67	1.90	0.389
Fe	ppm Fe	0.5-1	0.348	0.014	0.025	0.007
Zn	ppm Zn	0.1-0.2	**0.418**	0.064	0.112	0.087
TSS	ppm TSS	10-15	< 7	< 0.1	< 0.1	< 0.1

The abatement efficiencies for ammonia and nitrates are outlined in Table 4 and Figure 3. Starting with a water with relatively low input values for NH4+, both the VF tanks (95%) and the HF (99%) returned a very high culling. A rather low removal efficiency in the two vertical tanks (5.30 and 7.03% in the VFA and VFB respectively) was observed for NO_3, as the specific function of the vertical submerged flow tanks to transform the ammonia nitrogen in oxidized forms. On the other hand, the horizontal subsurface flow bed recorded an excellent NO_3 reduction (82%). Even in this case, the value obtained in this study was unexpected because several studies have observed that in the absence of sufficient organic matter (COD) the denitrification system is not efficient as indicated by Behrends et al. (2007), that performed a comparative investigation on several types of constructed wetland systems to decentralized treatment systems. Also Avila et al. (2013) in their study on an hybrid phytoremediation system, observed that concentrations of NO_x-N remained almost invariable along the horizontal tank, mainly due to the lack of organic matter necessary to heterotrophic bacteria In this study, the organic substance entering the CWs system had an average value of about 18 mg L^{-1}; a comparable situation was reported by Xinshan et al. (2010), but also by Masi and Martinuzzi (2007), who suggested to add organic matter to the system through recirculation, in a way to improve the overall performance of denitrification process. In doing so these authors managed to reach a 60% abatement rate. Another option suggested by Avila et al. (2013) is to regulate the HRT for a longer time: the condition is not very manageable in the VF systems, but easier with HF tanks. In our case, the four days of the retention time of the HF tank proved to be sufficient to allow an excellent denitrification process.



Figure 3 Main water parameters removal percentage (compared to inlet wastewater) for each CWs tank (VFA, VFB and HF).

The wastewater input was characterized by an average chloride concentration of 21.8±2.0 mg L^{-1}. The VFA and HF showed a capacity to reduce this concentration down to values of the order of 15.41±0.8 mg L^{-1}, obtaining a maximum reduction of 30%.

The concentration of sulfates in the inlet was 6.84±0.23 mg L^{-1}. Except for the values found in the first sampling, probably due to the earlier tests memory effect, the concentration of sulfates in the output from all the three tanks did not change significantly during the execution of the experiment with respect to the input value. The same behavior occurred for the concentration of sodium that started with an initial average value of 6.14±0.35 mg L^{-1} and remained similar in all the three outlet flows. For this parameter, a 20% abatement was recorded for the VF tanks, while for the horizontal one it did not exceed 8%.

The initial concentration of potassium was 2.01±0.15 mg L^{-1}; both vertical and horizontal systems recorded positive removal efficiencies with values around 5-15 % for the vertical tanks and slightly higher than 80% for the horizontal one. The wastewater entering the plant was characterized by an average concentration of calcium ion equal to 23.5±0.7 mg L^{-1}. As shown in Table 4 and Figure 4, the phytoremediation treatment determined significant increases in calcium concentration in the effluents from all the tanks. The concentration of such metal raised at about 40 mg L^{-1} for the VFB tank and between 50 and 60 mg L^{-1} for the VFA and HF tanks. This result, although not expected, justified the experimental evidence obtained for the electrical conductivity (a global increase of dissolved ions) and alkalinity (due to carbonate or bicarbonate presence). To understand if the cause of the calcium ion concentration increase could be the phytoremediation substrate, such material was tested in a leaching essay, whose results (Fig. 4) showed that the gravel used for filling the constructed wetlands bed was responsible for releasing calcium and aluminum.

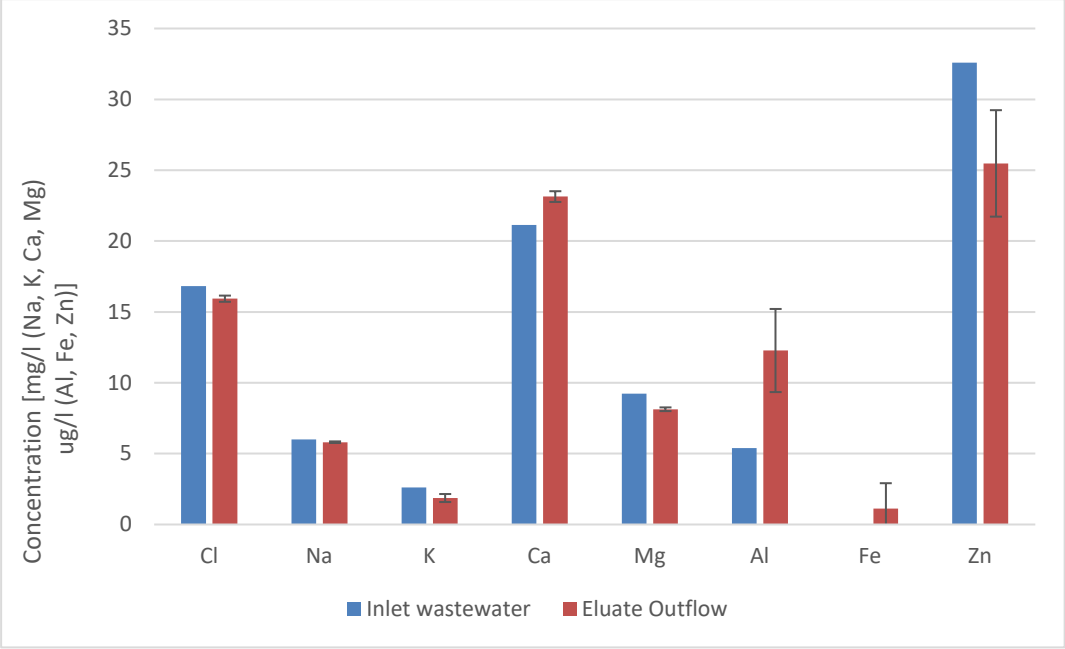


Figure 4 Comparison between the metal concentrations inside the inlet wastewater and the related eluate.

Chlorides, sodium, potassium, magnesium, and zinc were, to a greater or lower extent, retained. In contrast to what was observed for calcium, the phytoremediation plant was effective

in magnesium removal. In fact, its concentration decreased from an average initial value of 9.37±0.16 mg L^{-1} to values below 6 mg L^{-1} (VFA and VFB tanks). A different behaviour was found for the HF bed where, in the second part of the test, a rise in the magnesium concentration value was recorded. The average value was 6.69±0.12 mg L^{-1} with a reduction equal to 29%. A good efficiency was also recorded for the zinc removal since the output concentration (starting from a value of 418 µg L^{-1}) was steadily kept below 100 µg L^{-1}. On the other hand, the constructed wetland treatment had no influence on the aluminum removal. The wetland system showed excellent efficiency in removing iron: the initial concentration, 348±25 µg L^{-1}, was reduced (from HF tank) to values in the order of a few units (or fractions) of µg L^{-1}. TSS removal resulted very efficient for both type of systems (83.7, 98.9 and 99.2% for VFA, VFB and HF respectively) showing a positive contribution of the system in the entrapment of solids still present in the incoming wastewater. In Table 5 the parameters set by the EPA standards for the reuse of water in industrial processes and the results obtained in the phytoremediation test are compared. The columns labeled "Out VFA", "Out VFB" and "Out HF" show the average values of the parameters measured at the exit of the three different pools for the whole duration of the test. Figure 3 clearly shows that the best results, related to the considered scenario for the industrial reuse of treated wastewater, were obtained using the HF tank. This technology was then selected for evaluating its potential application at the Verrone plant.

3.2 Evaluating the potential application of HF at Verrone plant

Considering the results obtained in the experiments carried out at the pilot phytoremediation treatment system, two areas located within the FCA Verrone plant boundaries, that could be used for the construction of a full-scale phytoremediation plant, were selected. These areas have an available surface extension of 4,438 m^2 and 2,536 m^2 respectively. As shown in Figure 1, the average flow leaving the WWTP is about 540 m^3 d^{-1}. For the construction of a horizontal

subsurface flow system, it is necessary to evaluate the hydraulic loading rate according to the available area. Reed's method is the system most commonly used for the horizontal subsurface flow design and, therefore, it was selected as a reference for the design of the phytoremediation system in Verrone plant, mainly for the readiness of the results that can be predicted and consequently achieved. The Reed's method is recommended by the US Environmental Protection Agency (EPA) in the Constructed Wetlands guidelines and in Italy it is also suggested as a good reference for municipal WWTPs (ISPRA, 2012). The surface (As) was calculated as:

$$A_s = \frac{Q_{av}}{K \cdot d \cdot n} \cdot \ln\left(\frac{C_i}{C_o}\right)$$

In Reed's method, the elements that must be considered in the design are the substrate selection (conductivity and porosity), the areal demand for pollutant removal, the transversal area determination, the hydraulic retention time and the hydraulic loading rate. This method is based on a first order kinetics, where the depuration velocity is proportional to the substrate concentration. The method also assumes that the horizontal subsurface flow wetland works as a plug-flow reactor if the liquid pass through the tank substrate without mixing in the perpendicular direction. The model seems to be almost entirely independent of the temperature (only for the nitrogen species a sort of dependency is present) (Brix, 1997). Another useful method for the design of horizontal subsurface flow system is the Kadlec and Knight one (Kadlec and Knight, 1996). In this case the formula is as follows:

$$A_s = \frac{365 * Q}{KT} ln\left(\frac{C_{out} - C'}{C_{in} - C'}\right)$$

Where C_{in} is the concentration of considered pollutant entering in the system, C_{out} is the concentration of the considered pollutant at the exit of the system; C' is the concentration of the considered pollutant inside a natural ecosystem, K_t is the removal coefficient defined as follow:

$$KT = K_{20} \cdot \theta^{(T-20)}$$

With K_T as the removal coefficient at T temperature; K_{20} is the removal coefficient at 20°C; θ is the temperature correction factor. K_{20} is extremely variable as it depends on system characteristics, treatment technologies and weather conditions.

For the design of the constructed wetland it was decided to use the Reed's method, as it takes into account the granulometry of the substrate and therefore allows for a more precise configuration. The parameters used for dimensioning the system are listed in Table 6.

Table 6 Design parameters used with the Reed's equation for the two HF systems.

Design variables	Area "A"	Area "B"
Inlet Concentration (BOD – mg/L)	40	40
Outlet Concentration (BOD)	1	1
Water Temperature (°C)	12	12
Available area(m^2)	4,438	2,536
K_{20}	1.104	1.104
Porosity (%)	0.38	0.38
Substrate depth (m)	0.6	0.6

For the larger area, called "A", the useful flow was equal to 190 m^3 d^{-1}. Three 57x25 m tanks with parallel flow were assumed to use the available space, with a consequent hydraulic loading rate of 4 cm d^{-1}, HRT equal to 5.3 days and filtration rate of 4.1 m d^{-1}. All the obtained values were within the limits of acceptability and provided a good margin of safety. For the smaller area, referred to as "B", the construction of two tanks with parallel flow of 66x19 m was foreseen in order to treat an income flow of 110 m^3 d^{-1} keeping hydraulic loading rate, retention time and filtration rate to the same values defined for the area "A". Considering the dimensions of the two CW models that could be built in the two available areas, in the "A" area, from a minimum of 35% to a maximum of 50% of the effluents from the existing WWTP could be processed, while in the "B" area the above range of the treatable flow is limited to 20-29%. If case of activation of the CW systems in both areas, from 55% to 80% of the WWTP effluents could be processed (due to seasonal patterns), as shown in Figure 5.

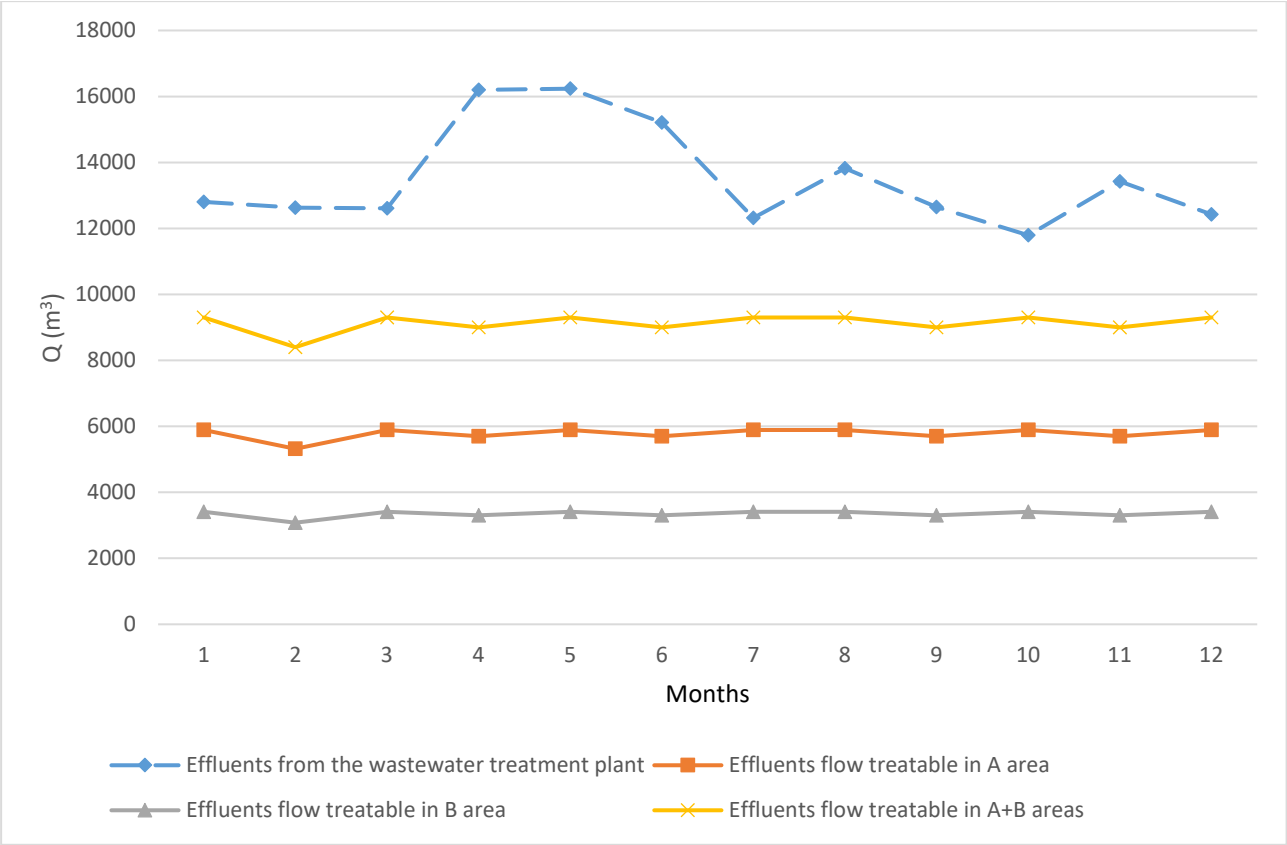


Figure 5 Average effluents flow from the existing WWTP for the years 2012-2013 and flow that could be processed by the horizontal subsurface flow tanks in the "A" and "B" area and by a combination of the two systems.

3.3 Cost considerations and comparison with a traditional system.

For evaluating the feasibility of constructing the HF phytoremediation system at Verrone plant an economical comparison between this technology and a traditional one was performed. In Figure 6 the flow diagrams of the two considered options are compared. The construction cost of both systems was estimated to treat the same input flow of 300 m^3/d from the Verrone WWTP.

The traditional process chosen for this comparison is composed of the following sequence of treatment sections:

Sand filtration: two parallel (one operating + one backwash) sand filters operating at a filtration velocity of 3 – 3.5 $m^3/d\ m^2$ for the removal of total suspended solids.

Ozonation: ozone generator, supplied by compressed air and cooled by water, constructed with stainless steel vertical tubes and designed to process 18 m^3/h of wastewater coming from the WWTP.

Activated carbon filtration: two parallel (one operating + one backwash) activated carbon filters working in parallel for the adsorption of mineral oils, surfactants, hydrocarbons, odours, flavours, yeasts and non-soluble substances.

Reverse osmosis and air stripping: A spiral wound type polyamide reverse osmosis membrane allowing to obtain a permeate to be reused as industrial water equal to about 70% of total flow-rate. The remaining 30% is a saline solution that it is fed back for treatment into the existing WWTP (see Figure 6).

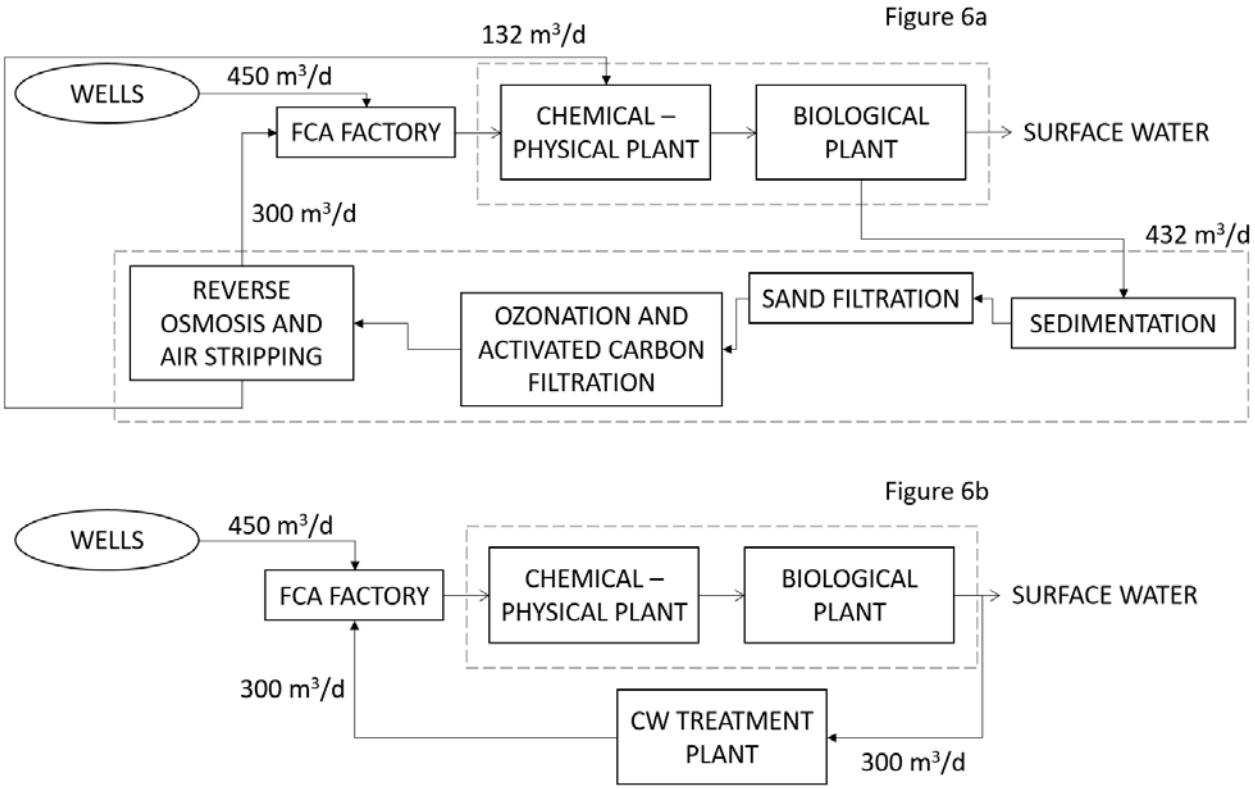


Figure 6 Graphical representation of a traditional and a constructed wetland wastewater treatment plants.

a Layout of a traditional plant for the treatment and reuse of industrial wastewater.

b Layout of the proposed constructed wetland system.

The cost estimate for the above described traditional treatment plant resulted equal to about 730 k€ for the construction of the plant, based on the 2016 Piedmont Region Public Works Pricelist. Marcucci and Tognotti (2002) indicated that the investment cost for a traditional plant

like the one considered here was around the 25% of its total cost. The operating costs (electricity, chemicals, membrane change and man-work) of the considered traditional treatment plant for the Verrone plant water reuse were evaluated based on literature estimation as indicated by Marcucci and Tognotti (2002), with the following fraction of total cost: electric energy 25%, chemicals 33%, membrane change 10%, man work 7%. With this consideration, the operation costs will be equal to 2,190 k€. The traditional treatment plant proposed for the Verrone plant will have an investment cost of about 0.66 €/m^3 and an operating cost of about 2 €/m^3 for a total cost of 2.66 €/m^3. Marcucci and Tognotti in their work indicated an investment cost of 0.18 €/m^3 and an operating cost equal to 0.54 €/m^3, but with a much higher treated flow rate than the one of the Verrone plant (1,100,00 m^3/y compared to 109,500 m^3/y).

For the HF phytoremediation plant construction, maintenance and management aspects were considered in the cost estimate too. The following items, extracted from the 2016 Piedmont Region Public Works Pricelist, were considered for estimating the construction costs: total excavation of the constructed wetland beds; total excavation for placement of discharge pipes; total excavation for pipe positioning output; waterproof sheet with installation; construction of embankments; geotextile with installation; installation of PVC, tubing, fences, sampling wells; resettlement of areas affected by the work; planting vegetable essences; tank storage. The pumping station, equipment for automation and monitoring system were prized separately. The cost estimate resulted equal to about 90 €/m^2, leading to an overall cost of 610 k€ considering both areas “A plus B” as indicated in Table 6. Higher costs can depend upon the possible variability of some technological aspects (water lifting and handling, the degree of automation and monitoring systems) chosen for the realization of the system. Operational costs are associated with maintaining the vegetal component, mowing weed species, operating charge and discharge systems and the mechanisms for the regulation of the water flows. The system also requires

constant monitoring (with a sampling of wastewater treated) to verify its operational efficiency. The operation costs are equal to 271 k€ for both areas. In this estimation, the costs related to the design and safety are not included, eventually, with the proposed HF phytoremediation plant the overall treatment cost will be about 882 k€ equal to 0,8 €/m^3.

In Table 6 the costs related to the traditional and phytoremediation systems for reusing for industrial purposes the effluents from the existing WWTP are compared. The traditional one has the highest cost per m^3 of incoming effluent treated, as the general complexity of this system and its operational costs are much higher than the ones required by the phytoremediation systems.

4. CONCLUSIONS

From the results obtained in this study, it can be concluded that phytoremediation is a suitable technology that can be applied for the reuse of WWTP effluents in industrial processes. The pilot treatment plant showed excellent efficiency in the removal of heavy metals (Fe and Zn) and suspended solids and a good efficiency in the reduction of the concentrations of magnesium, potassium, and chlorides. In addition, the water quality did not worsen in terms of sulfates and sodium content.

However, the electrical conductivity, alkalinity and calcium concentration parameters did not meet the requirements for reuse. The behaviour of these three parameters is strongly correlated, since their increase, compared to the fed wastewater, as demonstrated by the leaching test results, was caused by calcium transfer from the substrate used to fill the constructed wetlands. A careful selection of an adequate substratum is therefore recommended to solve the problem. Furthermore, the experimental results showed that only the horizontal bed technique is effective in the removal of nitrates, in agreement with literature data. In the specific case this technology could be gradually adopted, starting with the construction of the HF system in the smaller area ("B"), with a water recovery equal to about 3,000 m^3 per month. The second HF system could then

be implemented on the bigger available area (“A”), with an increase in the treated water that could lead to the reuse for industrial purposes of about 9,000 m^3 per month. The industrial reuse of this volume of water could allow a strong reduction of pumped clean water, and an immediate double economic advantage for the plant management as also the outlet flow will decrease according to with the rate of reuse. Another aspect to be taken into consideration is the costs comparison between the proposed phytoremediation technology and a traditional plant. The traditional plant has a total cost of investment of 2,920,000€ that is far higher if compared to the phytoremediation system one that cost 882,000€ and therefore, the CW system seems to be an attractive alternative. More generally the obtained results show that phytoremediation systems can be a suitable solution to “close” the industrial wastewater cycle. The experience carried out in the past years, mainly for primary or secondary wastewater treatment, today allows the designers to build constructed wetland systems able to work in a very efficient way.

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