INFLUENCE OF THE CHARACTERISTICS OF ORGANIC MATTER ON THE EFFICIENCY OF HORIZONTAL SUBSURFACE-FLOW CONSTRUCTED WETLANDS

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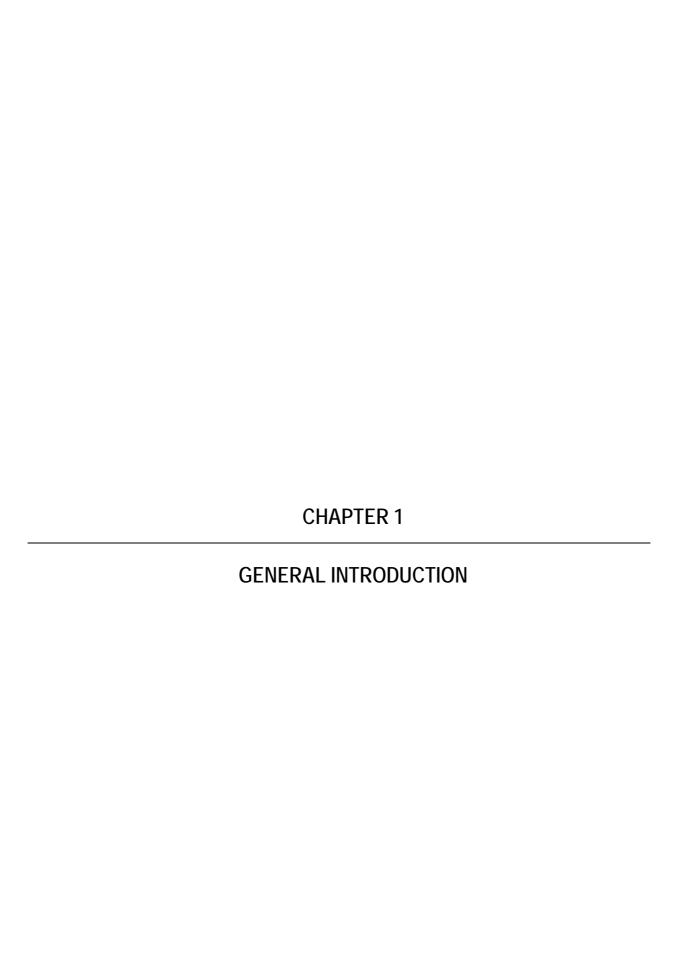




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Table of contents

Chapter 1	General introduction	ç
Chapter 2	Performance of experimental horizontal subsurface flow constructed wetlands fed with dissolved or particulate organic matter	19
Chapter 3	Effect of high organic loading rates of particulate and dissolved organic matter on the efficiency of shallow experimental horizontal subsurface flow constructed wetlands	35
Chapter 4	Effect of physico-chemical pretreatment on the removal efficiency of horizontal subsurface-flow constructed wetlands	49
Chapter 5	Impact of continuous and intermittent feeding strategy on the performance of shallow horizontal subsurface flow constructed wetlands	69
Chapter 6	Solids accumulation in five full-scale subsurface flow constructed wetlands	87
Chapter 7	General discussion	111
Chapter 8	General conclusions	119
Reference	es ·	123
Summary	(in English and Spanish)	137
Agradecir	nientos	143
Curricului	m vitae	147



1.1. GENERAL INTRODUCTION

There are many compelling reasons to develop cost-effective and sustainable wastewater treatment technologies in an era of escalating water shortages and world population growth. This dissertation analyzes a series of studies that were undertaken to better understand factors that affect the treatment efficacy of horizontal subsurface-flow constructed wetlands (SSF CWs) and to further develop design criteria. These studies are part of a comprehensive effort underway at the Technical University of Catalonia (Barcelona, Spain) to improve the design criteria and sustainability of shallow SSF CWs used to treat organic matter and nutrients in urban wastewater (García et al., 2004a, 2004b, 2005; Aguirre et al., 2005; Caselles-Osorio and García, 2006a). The following introductory pages briefly discuss the status of an ongoing freshwater crisis, the critical need for appropriate wastewater treatment systems, general information on SSF CWs, the processes involved in the removal of organic matter and nitrogen in SSF CWs, and pervasive problems related to the accumulation of solids in SSF CWs.

Escalating Worldwide Water Crisis

Today, a worldwide crisis is rapidly unfolding due to the declining supply of clean fresh water and the lack of adequate sanitation facilities. According to the World Health Organization (2005), 2.6 billion people live without proper means of sanitation and 1.1 billion live without access to improved drinking water. Lack of adequate water supplies and sanitation services causes 2 to 5 million deaths per year, and of these deaths, most are in underdeveloped nations, and the vast majority is of children afflicted with virulent diarrheas diseases (Gleick, 2004). As the world's population continues to grow and freshwater resources continue to be used and degraded, these problems will intensify. According to UNESCO (2006), by 2015, the worldwide water supply will be only one third the size required for the world's population. Because of these discouraging estimates, many cities and communities around the world are starting to adopt appropriate technologies and successfully promote water reclamation and reuse in order to preserve the limited high-quality freshwater supplies while helping to meet the ever-growing demand for water. In a recent survey, Mantovani et al. (2001) evaluated 65 international non-potable water reuse projects and documented their planning and management approaches. The authors of the survey predicted that in Israel, Australia and Tunisia the volume of reclaimed water will satisfy 25, 11 and 10%, respectively, of the total water demand within the next few years (Lazarova et al., 2001).

The Need for Alternative Systems

Most large cities around the world have technologically sophisticated, centralized wastewater treatment facilities. However, such facilities are not appropriate for smaller communities (< 2000 PE), rural villages and otherwise dispersed populations. Thus, there is a growing interest in the continued development and deployment of alternative and decentralized wastewater treatment technologies (Crites and Tchobanoglous, 1998). This interest is driven by economics and the plight of literally hundreds of millions of people who now live with substandard or nonexistent sanitation facilities.

Centralized treatment plants in large cities use energy-intensive processes and are designed to treat thousands of cubic meters of wastewater each day. These large plants require an extremely costly system of large-diameter sewerage pipes and pump stations to transport the wastewater, as well as highly trained around-the-clock operators. Many developing countries and rural communities urgently need small, decentralized systems that are less costly, less sophisticated and less energy-intensive. Alternative treatment systems differ significantly from conventional wastewater systems in that they are less energy-intensive, easy to operate and can be rapidly deployed (USEPA, 2000). The major advantages of decentralized and alternative technologies include the low capital costs associated with small-diameter sewerage pipes and the use of inexpensive treatment systems that incorporate natural processes such as stabilization ponds and constructed wetlands (Kadlec and Knight, 1996, Crites and Tchobanoglous, 1998).

Waste stabilization ponds and constructed wetlands are only two examples of the many types of "natural treatment systems" that are in use today. Others are described in Reed et al. (1995) and Crites and Tchobanoglous (1998), and include floating plant aquatic systems, submerged plant aquatic systems and land treatment systems (slow-rate and high rate infiltration, and overland flow). Natural systems can be used to attain wastewater treatment goals by using natural components and processes which significantly reduce the use of energy intensive mechanical devices. In general, use of natural systems can reduce the system system technical complexity, construction and energy costs.

Constructed Wetland (CW) Technologies for Wastewater Treatment: Background characteristics

Natural wetlands have been used as convenient wastewater discharge points for centuries. Pioneering research on constructed wetlands was conducted by European scientists (Seidel, 1966; Kickuth, 1977). Other major studies were conducted in the United States by Wolverton et al. (1983) and Gersberg et al.

(1984). In the ensuing years, a considerable amount of research has been carried out to improve design and operational criteria (USEPA, 2000; Kadlec et al., 2000). Since 1989, the International Water Association (IWA) has published the proceedings of ten international symposia on Wetland Systems for Water Pollution Control. Deployment and implementation of CW technology began to accelerate in the 1980s. Today, this technology is widespread around the world (Table 1). A recent survey and review of the literature reported that more than 1,640 wetland treatment systems have been constructed in the past 15 years in 19 countries (Wallace and Knight, 2006).

Table 1.1 Relation of systems put in operation in several European countries and the United States. FWS: Free Water Surface systems; SSF: Subsurface Flow systems

Country	Num	nber and type	CWs	- Reference		
Country	FWS	SSF	TOTAL	- Reference		
Portugal	4	296	300	Dias et al. (2006)		
France	*	400	400	Molle et al. (2005)		
Belgium (Flanders)	54	47	101	Rousseau et al. (2004a)		
Czech Republic	*	100	100	Vymazal (2002)		
Spain	12	27	39	Puigagut et al., submmited for publication		
United States	151	61	217	USEPA, (2000)		

^{*}Information not available

The book of Kadlec and Knight (1996) provide a comprehensive assessment of SSF CW technologies and other types of treatment wetlands. In general, constructed wetlands can be classified in two types: surface-flow (SF), and subsurface flow (SSF). In SF systems the wastewater flows across shallow ponds planted with aquatic macrophytes in direct contact with the atmosphere. SF systems are used primarily for treating secondary wastewater effluent and are generally designed with sufficient hydraulic retention time to ensure that the effluent is treated to tertiary standards. According to the direction of the flow, SSF CWs can be classified in horizontal-flow or vertical flow. SSF CWs are mainly designed to treat primary settled wastewater, although in some cases can be used to treat secondary effluents. In horizontal-flow systems, the wastewater is maintained at a constant depth and flows horizontally below the surface and through a granular media, such as gravel, which is planted with aquatic macrophytes. In vertical flow SSF system, the wastewater is distributed across the surface of the wetland, and trickles downward through the granular media, which is also planted with aquatic macrophytes. Vertical-flow systems perform in more aerobic conditions than the horizontal flow systems, and can accommodate higher organic- and ammonium- loading rates.

Horizontal SSF CWs, the subject of this dissertation, consist of relatively shallow beds (0.3 to 0.6 m deep) lined with non-porous clay or a synthetic liner and back-filled with granular media such as gravel. SSF CWs use plants that provide surface area for attached microbial growth and additional nutrient uptake (Kadlec et al., 2000). Figure 1 provides a conceptual diagram of a horizontal SSF CW and illustrates the placement of granular substrates and inlet and outlet pipes. In a SSF CW system setteable and particulate organic matter is removed using a septic or Imhoff tank before the wastewater is discharged to the wetlands. The length-to-width ratio of the beds is generally greater than 1:1, based on the assumption that this enhances plug flow conditions and treatment. However, several studies have shown that the aspect ratio has no significant effect on treatment efficacy (Bounds et al., 1998; USEPA, 2000). Hydraulic loading rate, surface organic load and water depth have been shown to be important design parameters (García et al., 2004b). Hydraulic retention time (HRT) is also an important parameter and can range from 2 to 15 days, depending on the strength of the wastewater and the desired effluent water quality (Kadlec et al., 2000).

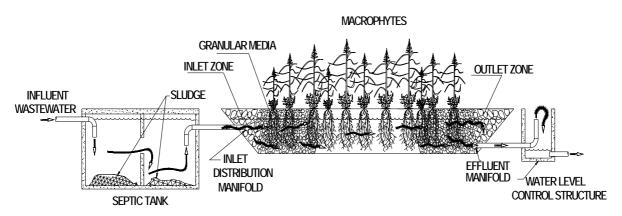


Figure 1.1 Conceptual diagram of a horizontal subsurface-flow constructed wetland with septic tank for primary treatment and outlet structure for water level control (drawing courtesy of Andre Koiman).

Removal Processes: organic matter and suspended solids

The removal of organic matter and the removal of suspended solids are concentration-dependent processes that can be modeled using generalized first-order removal rate equations with background concentrations (Kadlec and Knight, 1996):

$$A = \frac{Q}{K} Ln \left(\frac{C_o - C^*}{C_i - C^*} \right)$$

Where:

A is the surface area (m²)

C is the effluent concentration (mg/L)

C* is the background concentration of the parameter (mg/L)

Ci is the influent concentration (mg/L)

K is the first-order kinetic constant (m/d)

Q is the flow (m³/d)

The treatment mechanisms that occur in SSF CWs ensure that the effluent will have low concentrations of suspended solids, organic matter (BOD and COD), and depending on the design also of nutrients, metals and pathogenic microorganisms. Although the concept of constructed wetlands is often viewed as a simple process, the underlying treatment mechanisms are very complicated. Mass removal of pollutants is the result of a complex set of interacting physical, chemical and biological processes (Zitomer and Speece, 1993; Reddy and D'Angelo, 1997). Research and development activities continue to enhance the comprehension of these factors and provide advances in SSF technology (Kadlec and Knight, 1996; USEPA, 2000; Kadlec et al., 2000). However, there are still several critical knowledge gaps related to the removal of dissolved and particulate organic matter and factors influencing sediment buildup and long-term treatment sustainability.

In SSF CWs, suspended solids and particulate organic matter are removed quickly by means of physical processes such as sedimentation, adsorption and entrapment. Subsequently, the hydrolyzed portion of the particulate matter is oxidized by means of aerobic and anaerobic processes including aerobic respiration, denitrification, sulfate reduction and methanogenesis (Kadlec et al., 2000; García et al., 2004a). Dissolved organic matter can be adsorbed to granular media, plant roots and detritus and oxidized by resident microbial populations (Burgoon et al., 1995). These removal processes occur most frequently in the inlet zone. Over time, the deposition of refractory compounds, sloughed biofilms and mineral matter can have a negative impact on porosity and on the hydraulic behavior of the system (Fisher, 1990; Tanner et al., 1998). To reduce problems related to excess deposition, some authors have recommended limiting organic loading rates to 6 BOD₅/m².d for horizontal SSF CWs (USEPA, 2000; García et al., 2005). Some studies have also recommended a limit of 20 g TSS/m².d for SSF CWs (USEPA, 2000).

Accumulation of Organic Matter and Suspended Solids

The accumulation of particulate and dissolved organic matter in porous media such as sand, gravel or clay has been studied extensively in the fields of geology and groundwater hydrology (McDowell-Bayer, 1992; Rinck-Pfeiffer et al., 2000). The occlusion of pore spaces within the granular matrix of the SSF CWs occurs most frequently in the inlet zone, where influent suspended solids and extensive biofilm growth tend to accumulate and clog the interstitial spaces between gravel aggregates (Hansen et al., 2002; Langergraber et al., 2003). As noted above, particulate matter, dissolved organic matter and mineral matter are removed near the inlet by means of sedimentation, adsorption and entrapment within the biofilm. Rapid growth of microbial biofilms and plant roots occur in this region due to the nutrient- and mineral-rich influent. Over time, these chemical, physical and biological processes contribute to pore blockage and cause detrimental changes in the hydrodynamic behavior of the system, such as short-circuiting, reduction of hydraulic retention time, surface ponding of wastewater, odors, presence of insects, and potential reductions in treatment efficiency (Platzer and Mauch, 1997). Under worst-case scenarios, the life span of the wetland treatment system may be reduced to a few years. Although pore blockage is a common and pervasive problem in horizontal- and vertical-flow treatment wetlands, very few quantitative studies have been carried out to determine which factors contribute to the problem. Vertical-flow systems are more oxidized and are loaded at higher organic rates. These conditions are more conducive to sediment accumulation. With experimental vertical-flow systems loaded at 18.3 g COD/m².d, Behrends et al. (2006) reported pore blockage in which 30-68% of the pore void space was filled with recalcitrant organic sediments after 28 months of operation. Various noninvasive treatments for removing recalcitrant organic matter from SSF CWs have been evaluated, including air sparging and the use of concentrated hydrogen peroxide, nutrients, translocation by earthworms and commercial microbial formulations (Hansen et al., 2002; Davison et al., 2005). Replicated studies of several of these techniques, individually and in various combinations, are being conducted by the Tennessee Valley Authority (TVA) in Muscle Shoals, Alabama (Behrends et al., 2006).

Nitrogen Dynamics and Rate Limiting Processes

In wastewater treatment, the main biological nitrogen removal pathways include deamination of protein (ammonification), nitrification and denitrification (Kadlec and Knight, 1996). Less significant mechanisms include microbial assimilation, plant uptake and ammonium volatilization (Zhu and Sikora, 1995). In many reports horizontal SSF CWs have not provided significant nitrogen removal (Kadlec et al., 2000) because nitrification is severely inhibited by low dissolved-oxygen concentrations (<0.2 mg/L). At low-to-moderate

organic loading rates (2-8 g BODs/m².d), atmospheric oxygen diffusion, which is the major supplier of oxygen to SSF CWs, is often not sufficient to supply adequate amounts of oxygen for nitrification. However, recent research (García et al., 2004a) has revealed that shallow SSF CWs (0.27 m) remove organic matter and nitrogen with very high rates and better than deeper beds (0.5 m). The supporting data indicated that the shallower beds were more oxidized, possibly due to the shallow water and enhanced oxygen diffusion at the air-water interface. Although the role of wetland plants in net oxygenation of the root zone has been shown to be marginal (Brix and Schierup, 1990), plants do play an important role in evapotranspiration and nutrient uptake and provide a sustainable carbon source for denitrification (Kadlec and Knight 1996). However, additional studies are required in order to more fully understand the surface reareation process as a function of depth, loading rate and hydraulic retention time. This level of understanding is needed in order to design more effective SSF CWs.

Definition of the problem and objectives of the thesis

Although horizontal SSF systems are getting better at removing organic matter (80-90%) and total nitrogen (25-50%), certain serious and pervasive problems still need to be addressed. One major problem is the accumulation of organic and mineral matter in the interstitial pore spaces of the granular material. This occurs most frequently in the inlet zone and leads to reductions in hydraulic retention time (HRT), surface ponding, short circuiting, odors and finally a shorter useful life of the facility. Several factors may contribute to this problem, including the poor removal of settleable solids in the primary treatment, the improper design of the influent distribution lines and overload. The particulate matter contained in the primary effluent is composed of a mixture of substances of various sizes and compositions, including organic matter, silt and other inorganic chemicals. Furthermore, the composition of the organic matter and its relative biodegradability can impact the efficiency of wastewater treatment. Currently, there is very little practical information on how the characteristics of the influent wastewater and the physical state of the organic matter affect the efficiency and hydraulic properties of wetlands. The aim of this thesis is to provide answers to the following questions:

- How is the efficiency of experimental wetland systems affected by the type of organic matter (dissolved vs. particulate) in the wastewater influent?
- How do extreme organic loading rates (dissolved vs. particulate) influence treatment efficiency?
- Can a physico-chemical pretreatment of wastewater improve the efficiency of SSF CWs?
- How and to what extent does intermittent or continuous loading affect treatment efficiency?

 How do the quantity and quality of solids accumulated in wetland substrate affect hydraulic conductivity, treatment efficacy and long-term system sustainability?

1.2. OBJECTIVES

General objective

Horizontal subsurface-flow constructed wetlands (SSF CWs) are wastewater systems used mainly to treat urban wastewater to secondary effluent standards. Although SSF CWs are currently considered as a viable technology, improvements are needed in order to optimize treatment efficiency and extend the life-span of the system.

The initial hypothesis of this study was that settled urban wastewater still contains enough particulate organic matter to negatively affect the efficiency of wetlands treatment, hydraulic conductivity and long-term sustainability.

The main objective of the present investigation is to evaluate the near- and mid-term impact(s) of dissolved and particulate organic matter on the treatment efficiency of horizontal SSF CWs. These impacts will be ascertained under a wide range of experimental conditions with respect to hydraulic loading rates, organic loading rates, availability of electron acceptors and hydraulic regime.

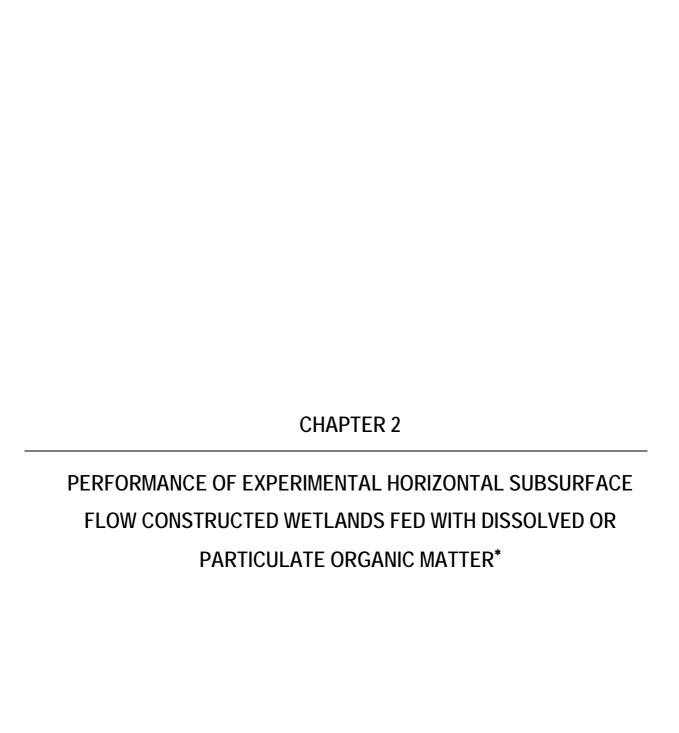
Specific objectives

In order to achieve this general objetive, several specific objectives were formulated:

- To determine the qualitative effect of the organic matter (dissolved and particulate) on the efficiency of experimental SSF CWs.
- To determine the effects of high organic loading rates, both of dissolved and particulate organic matter, on the treatment efficiency of experimental SSF CWs.
- To evaluate the effect of a physico-chemical pretreatment on water quality in experimental SSF CWs.
- To determine the effect(s) of intermittent and continuous wastewater loading on the removal of

- organic matter and ammonium nitrogen in experimental SSF CWs.
- To determine the amount and quality of accumulated solids in several full-scale SSF CWs (located in Catalonia, Spain) as a function of organic loading rate(s) and location (inlet, middle and outlet zones).

These objectives provide the basis for hypothesis development and experimentation, the results of which are discussed in the following chapters. The final chapter of this dissertation provides a general discussion, synthesizes the results and summarizes the major findings.



Caselles-Osorio, A. and García, J. 2006. Performance of experimental horizontal subsurface flow constructed wetlands fed with dissolved or particulate organic matter. Wat Res. (40/19), 3603-3611.

^{*} An early version of this chapter was published as:

2.1. ABSTRACT

In this study, the effect of the influent type of organic matter (dissolved or particulate) on the efficiency of two experimental horizontal subsurface flow constructed wetlands (SSF CWs) was investigated. The SSF CWs surface area was 0.54 m² and the water depth was 0.3 m. They were monitored for a period of 9 months. One of the SSF CWs was fed with dissolved organic matter (glucose, assumed to be readily biodegradable), and the other with particulate organic matter (starch, assumed to be slowly biodegradable). The removal efficiency of the systems was tested at different hydraulic retention times in the presence or absence of sulfate. The removal efficiency of the COD was not different in the two systems, reaching eliminations of around 85% in the presence of sulfates and around 95% in their absence. Ammonium N removal was low in the two SSF CWs; the system fed with glucose generally had statistically significant higher removal (45%) than the one fed with starch (40%). Ammonium N removal was more affected by the hydraulic retention time than by the presence or absence of sulfates. Hydraulic conductivity measurements showed that it was lower near the inlet of the SFF CW fed with glucose, probably connected to the fact that there was a more substantial development of the biofilm. The results of this study suggest that SSF CWs are not sensitive to the type of organic matter in the influents, whether it is readily (like glucose) or slowly (like starch) biodegradable, for the removal of COD.

2.2. INTRODUCTION

Horizontal subsurface flow constructed wetlands (SSF CWs) are low-cost treatment systems in which wastewater flows slowly across the gravel and the roots and rhizomes of the emergent planted vegetation. The removal of contaminants occurs as a result of complex physical, chemical and microbial interactions (Kadlec and Knight, 1996). The rates of these processes may vary in time and space, and depend on many factors such as the organic surface loading rate, the depth of the water and the availability of electron acceptors (García et al., 2004a; Aguirre et al., 2005).

Although SSF CWs have been used to treat a wide range of wastewaters, they are most commonly used to treat domestic and municipal wastewaters. One of the major objectives of these systems is the removal of the organic matter. Wastewaters contain complex mixtures of of organic matter of different size and types, from dissolved to particulate, and from readily biodegradable to inert constituents (Kadlec, 2003; Levine et al., 1991). Long term experience in conventional wastewater treatment systems has demonstrated that the size

frequency distribution function of the organic matter is a key factor in determining the removal efficiency (Sophonsiri and Morgenroth, 2004). Particulate organic biodegradable substrates (as well as high molecular weight dissolved and colloidal constituents) must undergo cell external hydrolysis before they are available for biodegradation (Gujer et al., 1999). This hydrolysis process can be one of the most limiting steps during the removal of organic matter either under anaerobic, anoxic and aerobic conditions (Mino et al., 1995; Ubukata, 1997; Sanders et al., 2000).

There is currently no experimental information available on the comparative effect of particulate and dissolved substrates on the removal efficiency of SSF CWs. Several reports, nevertheless, have recently discussed in a theoretical manner the possible effect of particle size distribution. For example, Kadlec (2003) inferred the removal efficiency of different contaminants as a function of their size and also of their physicochemical properties. Tchobanoglous (2003) pointed out the importance of organic matter size distribution as a design criterion, and reviewed pretreatment systems for reducing particulate substrates and therefore for modifying the size distribution function. Baptista et al. (2003) discussed the possible mechanisms for organic matter removal as a function of its size distribution function. In the present study we experimentally evaluated the removal efficiency of two identical experimental SSF CWs operated under the same conditions, but one fed with starch (as a slowly biodegradable particulate substrate) and the other with glucose (as a readily biodegradable dissolved substrate). The efficiency of the systems was tested using different hydraulic retention times as well as with the presence or absence of sulfate, which in previous studies has been observed to be an important electron acceptor in SSF CWs that treat municipal wastewaters with high sulfate content (Aguirre *et al.*, 2005).

2.3. MATERIAL AND METHODS

Experimental SSF CWs

SSF CWs were built using plastic containers (0.93 m long, 0.59 m wide and 0.52 m high) filled with wetted gravel extracted from a pilot SSF CW system located at Les Franqueses del Vallès, Barcelona, Spain. This pilot system started operating in 2001 (García *et al.*, 2004a). The containers had a drainage pipe located on the bottom of one of their sides. The bottom was flat. Gravel depth was 0.35 m (the diameter at which 60% of the material passed through the sieve was D_{60} = 3.5 mm, the uniformity coefficient was C_u = D_{60}/D_{10} = 1.7 and the initial porosity was 40%) and the water level was maintained at 0.05 m under the gravel surface to give a water depth of 0.30 m. In April 2004, reed rhizomes (*Phragmites australis*) were planted in the experimental

systems and stored in the Environmental Engineering Laboratory (Technical University of Catalonia, Barcelona) in order to avoid great temperature variations (Figure 2.1). In addition to environmental light, each experimental SSF CW was illuminated using 15 Grolux lamps that provided a total power of 540 W. Although plant cover was attained in two months, the reeds stems were thinner and shorter than is usually observed in the field.



Figure 2.1 Experimental SSF CWs fed with dissolved (glucose) or particulate (starch) organic matter. The experimental units were located in the laboratory of the Sanitary and Environmental Engineering Section of the UPC.

Influent preparation and experimental strategies

This study was carried out between April and December 2004 and four different experimental phases were established. Table 2.1 summarises the conditions under which the two SSF CWs were operated during these phases. One SSF CW was fed with an influent containing starch $(C_6H_{11}O_5)_n$ as slowly biodegradable organic matter and the other with an influent containing glucose $(C_6H_{12}O_6)$ as readily biodegradable organic matter (Mino *et al.*, 1995; Gujer *et al.*, 1999). Throughout all the phases, the surface organic loading rate was maintained approximately constant and identical in both SSF CWs. Thus, 3.8 g of starch or 4.0 g of glucose were added on a daily basis to the water volume that was used as influent (10 or 20 L of tap or distilled water, depending on the phase). The weights of the starch and glucose were calculated in order to have the same theoretical influent COD concentration in both SSF CWs. For glucose the amount was estimated using the stoichometric relation to the oxygen necessary for its oxidation. In the case of starch, a calibration curve between the starch mass and the COD was obtained and used. Major nutrients were supplied by adding 1.0

g of NH₄Cl and 0.09 g of KH₂PO₄ to the influent. All these amounts were calculated to have a C:N:P ratio of approximately 100:16:1. Influent water was prepared daily.

Table 2.1 Operational conditions used for both SSF CWs in the 4 different experimental phases. One SSF CW was fed with starch, the other with glucose. The values of COD and NH₃ concentrations and surface loading rates are based on theoretical calculations.

		Phase						
	I		III	IV				
Date	May-Jun 04	Jul-Sep 04	Sep-Nov 04	Nov-Dec 04				
Water used for influent	Tap	Tap	Distilled	Distilled				
Flow, L/d	20	10	10	20				
Hydraulic retention time, d	3	6	6	3				
Influent COD concentration, mg/L	150	300	300	150				
Surface loading rate, g COD/m ² .d	6	6	6	6				
Influent NH ₃ concentration, mg N/L	13	26	26	13				
Presence of SO ₄ ² -	Yes	Yes	No	No				

The different experimental phases were established in order to compare the removal efficiency of the SSF CWs for different hydraulic retention times (HRT) and in the presence or absence of sulfates in the influent. Thus, two different HRTs (3 or 6 days) were applied in combination with two different influent water sources (tap or distilled). The tap water used in this study is characterised by its high salinity (>1000 μ S/cm), high sulfate content (>150 mg/L) and very low levels of organic matter and nutrients (AGBAR, 2004). The distilled water had undetectable sulfate concentrations (less than 1 mg SO₄²-/L, which is the limit of detection). HRT was controlled by means the influent flow rate (10 or 20 L/d). Both SSF CWs were fed in batch form; thus, the daily flow was added for a 20 min period at one side of the SSF CWs. Batch operation was used instead of continuous operation because in previous trials it was observed that starch settled very rapidly and adsorbed onto the walls of the tanks and pipes. Batch operation therefore made it possible to reduce variations in the COD mass loading rates in the SSF CW fed with starch. Measurements started 20 days after the feeding of the SSF CWs had begun.

Each phase lasted approximately two months. Three influent and effluent samples were taken weekly and analysed immediately for temperature, turbidity, dissolved oxygen (DO), sulfate, nitrate, Ammonium N, and chemical oxygen demand (COD). The temperature was measured with a Chektemp-1 Hanna thermometer, the turbidity with a Hach 18900 turbidimeter, and the other parameters were analysed using conventional

methods as described in APHA-AWWA-WPCF (2001). Effluent samples were obtained from the water volume displaced (stored in a vessel) when the influent was added.

Hydraulic conductivity tests (HCTs)

At the end of the experiments, HCTs were carried out near the inlet and the outlet of the two SSF CWs (in exactly the same position) in order to examine the effect of the substrates on the hydraulic conductivity of the granular medium. The method described in NAVFAC (1986) as the falling head test was used. HCTs were performed by means of a plastic tube that was 0.48 m long and 0.2 m in diameter, which was vertically inserted 0.2 m into the gravel. Subsequently, 8 to 10 L of tap water were poured into the tube in a pulse and the variation in pressure was monitored using a Druck PTX 630-1525 (0-5 m) probe connected to a computer by means of a Datataker DT50. The probe was placed inside the tube on the gravel surface; therefore, pressure variations were proportional to the water column height inside the tube. Measurements were obtained every second. The hydraulic conductivity was estimated by means of the equation described in NAVFAC (1986), which is obtained by combining the mass conservation principle and Darcy's law:

$$K = \frac{d^2 \ln(2L/d)}{8Lt} \ln \frac{h_1}{h_2}$$

where:

K is the hydraulic conductivity, in m/s h_1 is the initial water height inside the tube, in m h_2 is the water height inside the tube at time t, in m d is the diameter of the tube, 0.2 m L is the length of the tube which is submerged, 0.15 m t is the time, in s.

To estimate the hydraulic conductivity, an iterative procedure was used together with least squares fitting. Residuals were obtained from the difference betwen the theoretical h₂ values and the field data. Note that the hydraulic conductivity found using this method is in fact "apparent"; therefore, the values can not be compared to others obtained in different systems. This is due to the small size of the experimental SSF CWs, which caused a certain rise in the water level instead of allowing complete horizontal displacement to take place.

Microscopical observations of the interstitial water near the inlet were regularly carried out using a Nykon Eclipse 50i microscope. Samples were collected before feeding.

The COD and Ammonium N removal efficiencies were calculated as percentages. Note that volumetric removal rates gave almost identical values as percentage removals. Statistical procedures were carried out using the SAS statistical software package. One and three way ANOVA methods were used to check the influence of the type of organic matter supplied (glucose or starch), the HRT (3 or 6 days) and the presence or absence of sulfates on the removal efficiency of the SSF CWs.

2.4. RESULTS

The mean values and standard deviations of water temperature, turbidity, DO and sulfate are shown for the different phases in Table 2.2. Water temperature was identical in the effluents of both SSF CWs in all four phases. The average temperature had a minimum value in phase IV and a maximum value in phase II. Turbidity was higher in the influent of the SSF CW fed with starch due to the particulate nature of the starch. Note that in phases II and III the turbidity of the influent starch solution was approximately twice as high as in phases I and IV because the same amount of starch mass was added to only half the volume of water. Starch was well retained in all phases as indicated by the low turbidity in the effluent.

Table 2.2 Mean values and standard deviations (in brackets) of the water temperature, turbidity, dissolved oxygen and sulfate in the experimental SSF CWs fed with glucose and starch in the different phases. Calculations were made using 26 samples in phase I, 24 in II, 19 in III and 21 in IV."nm" not measured.

Phase	Temperat	ure (°C)	-	Turbidity (NTU)		DO (mg/L)			SO ₄ 2- (mg/L)					
	Glucose	Starch	Glu	cose	Sta	ırch	Glu	cose	Sta	arch	Glud	cose	Sta	irch
	Eff	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff
1	21	21	0.4	0.8	12	0.9	7.4	< 0.05	8.4	< 0.05	170	57	170	52
ı	(2)	(2)	(0.1)	(0.4)	(8.0)	(0.2)	(0.7)	(-)	(0.7)	(-)	(28)	(29)	(28)	(32)
п	25	25	0.8	0.5	26	8.0	6.4	< 0.05	7.9	< 0.05	160	40	160	50
II	(0.6)	(0.6)	(0.5)	(0.2)	(2)	(0.4)	(0.7)	(-)	(1)	(-)	(36)	(25)	(32)	(22)
Ш	22	22	0.4	0.5	24	0.6	6.8	< 0.05	8.6	< 0.05	n 100	n 100		
III	(1.7)	(1.7)	(0.1)	(0.1)	(3)	(0.3)	(0.4)	(-)	(0.5)	(-)	nm	nm	nm	nm
11.7	19	19	0.2	0.8	14	1.0	8.6	< 0.05	8.8	< 0.05	n 100	n 100		
IV	(8.0)	(8.0)	(0.1)	(0.3)	(1)	(0.7)	(0.5)	(-)	(0.4)	(-)	nm	nm	nm	nm

Influent DO and sulfate concentrations were very similar in the two SSF CWs. The same trends were also observed in the effluents: DO was not detected in the effluents of the two SSF CWs and approximately the

same amount of sulfate was removed. The systematic lack of DO and lower effluent sulfate concentrations than in the influent indicate that both SSF CWs had strong reducing conditions. Nitrate concentrations in both SSF CWs were lower than 2 and 0.5 mg N/L in the influent and effluent respectively. The influent nitrate contribution to the oxidation of organic matter is therefore considered irrelevant.

Figures 2.2 and 2.3 shows the changes over time of the COD and Ammonium N concentrations in the influent and the effluent respectively. The mean concentration values, standard deviations and mean removal efficiencies of COD and Ammonium N are shown for the different phases in Table 2.3. Influent COD concentration was slightly lower in the SSF CW fed with starch due to the inevitable settling and adsorption of matter in the vessel used for the feeding process. In phase I the effluent COD concentration was similar in the two wetlands, while during the phases II and III the SSF CW fed with starch had slightly lower values. In phase IV, effluent COD concentrations were below the detection limit in all cases. In the two SSF CWs the lower effluent COD concentrations were obtained in the absence of sulfate in the influent. Note that in each period, the differences in the COD removal percentage for the glucose and starch systems were very low.

Table 2.3 Mean concentration values, standard deviations (in brackets) and mean removal efficiencies (Rem) of the COD and ammonium N in the experimental SSF CWs fed with glucose and starch in the different phases. Calculations were made using 26 samples in phase I, 24 in II, 19 in III and 21 in IV.

Glucose Starch Glucose Starch Phase Inf Eff Inf Eff Inf Eff Inf Eff Rem Rem Rem Rem COD COD COD COD NH₄-N NH₄-N NH₄-N NH₄-N (%) (%) (%) (%) (mg/I)(mg/l)(mg/l) (mg/I)(mg/L)(mg/L) (mg/L) (mg/L) 12.3 7.6 170 41 150 45 11.6 8.3 ١ 76 70 29 38 (10)(10)(17)(17)(3) (1.6)(2.6)(1.8)330 40 300 25 23.1 10.0 23.4 10.9 88 91 53 Ш 57 (38)(17)(2.7)(2.9)(2.5)(42)(13)(1.9)360 31 300 18 25.9 11.7 26.6 14.2 Ш 91 94 54 48 (5.4)(2.0)(2.9)(22)(18)(56)(9)(2.5)12.9 150 < 10 130 < 10 7.6 13.1 10.5 IV >94a >94a 41 20 (27)(1.1)(1.2)(2.1)(5)(-)(-)(1.6)

^a The actual value can not be calculated because low concentrations effluent COD.

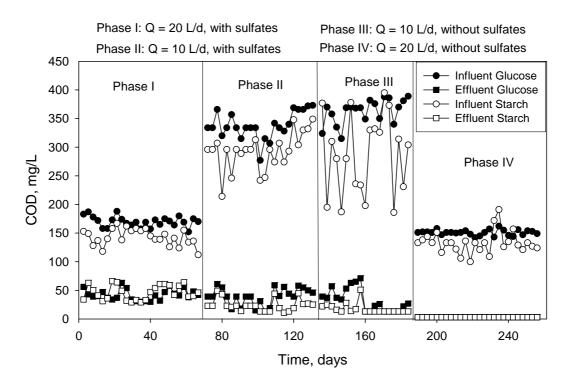


Figure 2.2 Changes in time of the influent and effluent COD concentration in the SSF CWs fed with starch and glucose.

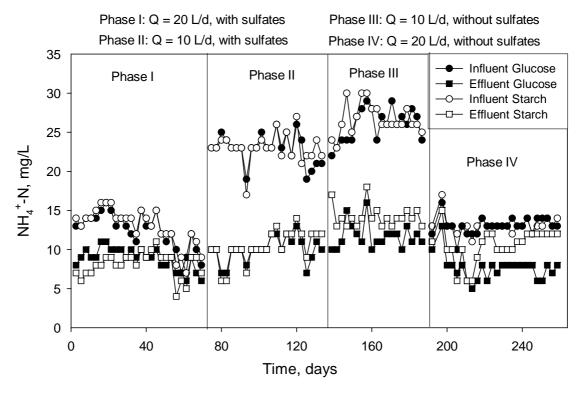


Figure 2.3 Changes in time of the influent and effluent ammonium N concentration in the SSF CWs fed with starch and glucose.

Ammonium N removal was generally low in the two SSF CWs and it was clearly affected by the HRT. Thus, the two SSF CWs had the highest removal rates in phases II and III when the HRT was 6 days. However, at the same time it should be pointed out that effluent concentrations were also higher in these phases. In phases I and II the effluents of the two SSF CWs had very similar ammonium N concentrations, while in phases III and IV, the system fed with glucose systematically had slightly lower concentrations.

The ANOVA test on the efficiency of the COD and ammonium N removal was performed taking the following three factors into consideration: the type of substrate (glucose or starch), the HRT (3 or 6 days) and the presence or absence of sulfate, and their interactions (Table 2.4). The type of substrate did not result in statistically significant differences in the removal efficiency of the COD. The interactions observed for the COD removal i.e. substrate*HRT and substrate*sulfates were due to the differences in performance iduring phase I (3 days HRT and presence of sulfates), when the SSF CW fed with starch had the lowest efficiency (see Table 2.3). Statistically significant differences of COD removal as a function of HRT are also connected to this first phase (that compensates for the higher efficiencies obtained in phase IV, and therefore reduces the average removal efficiency for an HRT of 3 days). The removals attained in the two SSF CWs in the absence of sulfates were higher than when they were present and were statistically significant.

Table 2.4 Probabilities of the ANOVA test on the effects of the factors (one-way) and their interactions (three-way) on the removal efficiency of COD and ammonium N.

	Substrate	HRT	SO ₄ 2-	Substrate*HRT	Substrate*SO ₄ 2-	HRT*SO ₄ 2-	Substrate*HRT*SO ₄ 2-
COD	0.0808	0.0001a	0.0001a	0.0003a	0.0479a	0.0001a	0.2569
NH ₄	0.0019a	0.0001a	0.0086a	0.4550	0.0001a	0.6704	0.0001a

^aStatistically significant differences at a significance level of "0.05".

This result is rather unexpected because sulfate reducing bacteria can compete with methanogenic bacteria and are more efficient for substrate removal (Kalyuzhnyi and Fedorovich, 1998; Hidalgo and García, 2001). The reason for this result may be the sulphide toxicity which has been observed to affect both sulfate reducing and methanogenic bacteria in anaerobic reactors (Kalyuzhnyi and Fedorovich, 1998; Kuo and Shu, 2004). In a recent study on sulfate reduction in SSF CWs, it was observed that when influent concentrations were above 75 mg SO₄2-/L, the organic matter removal decreased in a 20% and it was concluded that this may be related to sulphide toxicity (Wiessner *et al.*, 2005b). Note that in our study, the influent sulfate concentration was greater than 160 mg SO₄2-/L during phases I and II.

The type of substrate resulted in significant differences in the removal of ammonium N. As can be seen in Table 2.3, ammonium removal was higher in the SSF CW fed with glucose with the exception of phase I. This may be related to a greater heterotrophic microbial growth in the presence of a readily biodegradable compound such as glucose (in comparison to starch). The HRT and sulfates affected ammonium removal significantly. Ammonium removal was higher in the absence of sulfates in the case of the glucose experimental system. This fact coincides with higher COD removal efficiency during the same period. The interaction between the substrate and sulfates is due to the lower removal rates in the SSF CW fed with starch when no sulfates were present, in comparison to the results obtained in the presence of sulfates. The analysis of the results shows that the higher the HRT the higher the ammonium removal efficiency.

Microscopical observations of the interstitial water near the inlet revealed that in the SSF fed with starch there was a certain degree of accumulation of starch granules (Figure 2.4). In the SSF fed with glucose the biofilm seemed to be more compact and developed than in the SSF fed with starch.

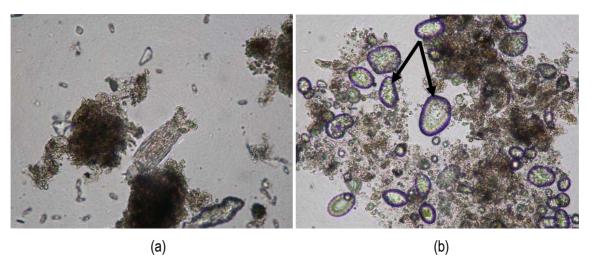


Figure 2.4 Image of the interstitial water in the SSF fed glucose (a) and starch (b). Note the starch granules indicated by the arrows.

The estimated values of the hydraulic conductivity were slightly higher in the inlet zone of the SSF CW fed with starch (28 m/d) than in the SSF CW fed with glucose (18 m/d). Near the outlet, the values were identical for the two SSF CWs (28 m/d). These "apparent" values are in fact somewhat lower than the actual hydraulic conductivity rate due to the small size of the SSF CWs; however, they can be compared between them.

2.5. DISCUSSION

The results of our research demonstrate that SSF CWs fed with different organic substrates (particulate slowly biodegradable and dissolved readily biodegradable) and operated using the same surface organic loading rates yield similar removal efficiencies of the COD under different HRT conditions and in the presence or absence of sulfates. In fact, the overall COD removal efficiency was not statistically different in the two experimental SSF CWs tested. This trend contrasts with the observations made in conventional wastewater treatment systems, in which it has been observed that the treatment efficiency is influenced by the type of substrate, particulate or dissolved (Särner, 1981; Levine et al., 1991; Sophonsiri and Morgenroth, 2004). In SSF CWs, the presence of a granular medium results the entrapment and sedimentation of solids (due to the low hydraulic surface loading rates), which make it possible to remove a high proportion of particulate substrate (Kadlec *et al.*, 2000). Starch is a polymer whose size ranges between 2 and 150 µm and behaves like settleable particulate organic matter (DEFRA, 2002; Sanders et al., 2000); it is therefore retained in the granular medium. However, it should be taken into account that the capacity for removing particulate matter observed in the experimental SSF CWs may be changed over time. Tanner et al. (1998) observed that the retention rates of solids were higher during the first years of operation than in subsequent years.

Microspical observations in the SSF fed with starch indicated that most of the starch was retained near the inlet. It can be reasonably assumed that in the starch-fed SSF CW, most of the starch was retained near the inlet, as has been described for particulate matter in SSF CWs treating municipal wastewater (García et al., 2004a; Tanner et al., 1998). After being retained, starch is hydrolysed and the net accumulation depends on the difference between the input and the hydrolysis rates. Mino et al. (1995) reported a starch hydrolysis rate of 32.2 mg/L.min in batch experiments under anaerobic conditions performed at 28 °C. Sanders *et al.* (2000), in similar experiments, indicated a surface removal rate of 0.4 g/m².h for anaerobic reactors operated at 30 °C. According to these values, and in view of the fact that for the purposes of this present study 3.8 g of starch were added per day, it was unlikely that the starch would have accumulated in the system. However, the temperature of the water in the experimental SSF CWs was lower than that used in the references referred to; therefore, the conditions were not as favorable for starch hydrolysis.

The hydraulic conductivity measured near the inlet was higher in the SSF CW fed with starch, despite the possible retention and accumulation of starch. In the system fed with glucose, the growth and development of biofilm was probably greater (and more concentrated near the inlet) than in the system fed with starch as

glucose is a carbon source readily biodegradable available. It is likely that the similar hydraulic conductivity in the outlet of both wetlands was due to the fact that less biofilm developed in these zones. These results suggest that biofilm growth is an important parameter in the evaluation of clogging phenomena. In general, studies on this issue do not take biofilm growth into account, and are only based on the retention of solids (Zhao et al., 2004).

The lack of DO in the effluents and the high removal rate of sulfates (in phases I and II) in the two SSF CWs indicate that the water inside the wetlands had strong reducing conditions. Thus, it could be reasonably assumed that the main mechanisms involved in the removal of organic matter are anaerobic pathways such as methanogenesis and sulfate reduction. Denitrification seemed to be a minor pathway in these systems given the low ammonium removal rate as well as the influent's low nitrate content. Considering that all ammonium is converted into nitrate and using the stoichometric calculations as described in García et al. (2004a) denitrification is responsible for removing a maximum of 15 % of the influent organic matter in the SSF CW fed with glucose (observed in phase II) and 14 % in that fed with starch (observed in phases II and III). Note that using this calculation procedure, the denitrification rates are overestimated as plant uptake and ammonium adsorption are not taken into account. The importance of sulfate reduction and methanogenesis for the removal of organic matter in SSF CWs has been already pointed out by Baptista et al. (2003), who estimated that approximately 60 % of the organic carbon was removed by these two metabolic pathways. In the present study these reactions may jointly account for an average of approximately 85 % in the SSF CW fed with glucose and 83 % for that fed with starch in phases I and II. In phases III and IV, the SSF CWs showed better removal efficiency in the absence of sulfates and methanogenesis alone may account for 84% of the influent organic matter in the SSF CW fed with glucose and 85 % in that fed with starch. However, it should be pointed out that the rates for these pathways are probably slightly overestimated as the organic matter mass retained in the granular medium by filtration and adsorption was not taken into consideration in making calculations. Lower COD removal efficiencies in the presence of sulfates (phases I and II) observed in the two SSF CWs may be related to sulphide toxicity, as has been suggested by Wiesser et al. (2005b). Sulphide greatly inhibits the growth of most anaerobic bacteria (Kalyuzhnyi and Fedorovich, 1998; Kuo and Shu, 2004).

The values of the first-order volumetric constant rates for COD removal at operating temperature (k_v) and at 20°C ($k_{v,20}$) are shown in Table 2.5 for all the various phases in the two experimental SSF CWs in order to compare them with the values quoted in other studies. For the calculation of these rates, it was assumed that the SSF CWs behaved like plug flow reactors with axial dispersion and with open-open boundary conditions

(García *et al.*, 2004b). The values of the dispersion number were obtained by injecting a non-reactive pharmaceutical product (clofibric acid) and the results were 0.031 for the SSF CWs feed with glucose and 0.044 for that feed with starch (Matamoros *et al*, unpublished data). These numbers are well within the range quoted by García *et al.* (2004a) for several SSF CWs. The values of the first order rate at operating temperature were obtained using an iterative procedure for solving the following equation (Crites and Tchobanoglous, 1998):

$$\frac{C}{C_o} = \frac{4 \cdot a \cdot e^{(\frac{1}{2}D)}}{(1+a)^2 e^{(\frac{a}{2}D)} - (1-a)^2 e^{(-\frac{a}{2}D)}}$$

Where,

C is the effluent COD concentration, mg/L

Co is the influent COD concentration, mg/L

a is $\sqrt{1+4k_VtD}$, dimensionless

D is the dispersion number, dimensionless

t is the hydraulic retention time, d.

k_√ is the first-order volumetric kinetic constant at operating temperature, d-1

The values of the first order rate at 20 $^{\circ}$ C ($k_{v,20}$) were obtained using Arrhenius equation (Metcalf & Eddy, 2003):

$$k_{v,20} = \frac{k_v}{\theta^{(T-20)}}$$

Where,

 θ = 1.04 is the temperature coefficient, dimensionless

T is the operating temperature, in °C.

Table 2.5 Values of the COD removal first-order volumetric constant rates at operating temperature (k_v) and at 20 °C ($k_{v,20}$ d⁻¹) for both experimental SSF CWs and in the different phases.

Phases	Glu	ıcose	St	arch
	k _v	k v,20	kν	k v,20
1	0.51	0.49	0.46	0.44
	0.44	0.36	0.52	0.43
III	0.54	0.50	0.68	0.62
IV	>1.44 a	>1.50a	>1.50 a	>1.60a

ak_v and k_{v,20} can not be given exactly because the effluent COD was under the detection limit.

Note that the average influent and effluent COD obtained in the different phases were used for these calculations. The $k_{v,20}$ values are similar for both substrates, as is to be expected given their similar removal efficiencies. These values are also well within the range of magnitude found in previous studies reviewed by Rousseau et al. (2004b). First order rate constants, for the moment, seem to be the best available design tool for SSF CWs, but the values to be used should be selected from SSF CWs operating with similar conditions as it is expected for the system under design (Rousseau et al., 2004b).

In contrast to the high COD removal rates observed in the two SSF CWs, ammonium N removal was generally quite low. In addition, ammonium N removal efficiencies were significantly different in the SSF CW fed with glucose and that fed with starch. SSF CW fed with glucose had higher ammonium removal rates. This may be related with a higher degree of ammonium assimilation by heterotrophs in the SSF CW fed with glucose because it is a readily biodegradable compound and favors more the heterotrophic growth in comparison to starch.

The ammonium N removal efficiency was highly dependent on the HRT, but this was not the case for the COD. García et al. (2004a) reported that the COD removal efficiency was more influenced by the redox status than by the HRT. Ammonium removal might have been more affected by the HRT than COD in the present study because processes such as nitrification have slower rates than those involved in the removal of the COD (Reddy and D'Angelo, 1997).

2.6. CONCLUSIONS

The two identical experimental SSF CWs, one fed with glucose and the other with starch, were almost equally efficient for the removal of COD under different HRT conditions and in the presence or absence of

sulfates during their first year of operation (70-94%). Thus, SSF CWs are not sensitive to the type of organic matter in the influents if it is readily (like glucose) or slowly (like starch) biodegradable for the removal of COD. The biofilm was apparently more developed in the glucose-fed SSF CW and in turn near the inlet its greater development seemed to reduce slightly the hydraulic conductivity in comparison to the SSF CW fed with starch.

Sulfate reduction and methanogenesis seemed to be the most effective metabolic pathways for removing organic matter. The highest COD removal efficiencies were obtained in the absence of sulfates in the influents. This may be related to the toxic effects of sulphide released during the activity of sulfate reducing bacteria.

The removal of ammonium N was slightly higher in the glucose-fed SSF CW (45% overall in comparison to 40% for the starch-fed SSF CW), which is probably related to a greater heterotrophic microbial growth in the former SSF CW.

CHAPTER 3

AND DISSOLVED ORGANIC MATTER ON THE EFFICIENCY OF SHALLOW EXPERIMENTAL HORIZONTAL SUBSURFACE FLOW CONSTRUCTED WETLANDS*

Caselles-Osorio, A., Porta, A., Porras, M. and García, J. Effect of high organic loading rates of particulate and dissolved organic matter on the efficiency of shallow experimental horizontal subsurface flow constructed wetlands. Water, Air, & Soil Pollution.

^{*} An early version of this chapter was submmited as:

3.1. ABSTRACT

Two experimental subsurface-flow constructed wetlands were operated at relatively high organic loading rates (22 g COD/m².day) for four months to evaluate their relative ability to remove either dissolved organic carbon (glucose, considered to be a readily biodegradable substrate) or particulate organic carbon (starch, considered to be a slowly biodegradable substrate). The systems were built using plastic containers (0.93 m long, 0.59 m wide and 0.52 m high) that were filled with an 0.35 m layer of wetted gravel ($D_{60} = 3.5$ mm, uniformity coefficient $C_u = D_{60}/D_{10} = 1.7$) and the water level was maintained at 0.05 m under the gravel surface to give a water depth of 0.30 m. The results indicated that there was no significant difference in COD removal between the two systems. Both systems generally had COD removal rates of over 90%, which is quite high if the heavy load applied is taken into account. The removal of ammonium was greater in the glucose-fed system (57%) in comparison with the starch-fed system (43%). Based on mass balance calculations and stoichiometric relationships, it was estimated that denitrification and sulphate reduction were minor pathways for the removal of organic matter. Indirect observations allowed to assume that methanogenesis made a highly significant contribution to the removal of organic matter.

3.2. INTRODUCTION

Horizontal subsurface-flow constructed wetlands (SSF CWs) constitute an appropriate technology for treating wastewaters that have been subjected to primary clarification. The use of SSF CWs is especially well suited to the removal of suspended solids, organic matter and nitrogen. The removal of suspended solids is very rapid, localized and efficient (85-90%), and is largely a physical process involving sedimentation and filtration. The ensuing biological treatment of dissolved and particulate organic matter and nitrogen involves a variety of complex processes that depend on the environmental conditions (anaerobic, anoxic and aerobic) (Kadlec and Knight, 1996). Aerobic respiration, denitrification, sulphate reduction and methanogenesis are the principal biochemical reactions involved in the oxidation and net removal of organic matter in these systems (Baptista et al., 2003; Reddy and D'Angelo, 1997; Burgoon et al., 1995).

It has been well documented that the surface area organic loading rate is one of the critical parameters affecting treatment efficacy, effluent water quality, and system life-span (Cooper et al., 1996; USEPA, 2000). For example, if the organic loading rate is too high, particulate organic matter and microbial biomass will accumulate more rapidly than is usual in the inlet area, causing a rapid and significant reduction in porosity,

and subsequent changes in hydrodynamic behaviour. In order to avoid these problems, Platzer and Mauch (1997) and USEPA (2000) have recommended that the organic loading rate should not exceed 25 g BOD/m².d in vertical-flow SSF CWs. In comparison, the loading rate in horizontal systems should not exceed 6 g BOD/m².d (USEPA, 2000; García et al., 2005).

In SSF CWs, it has been observed that the total organic matter concentration decreases rapidly near the inlet and little additional removal occurs beyond this area (Kadlec, 2003). This is due to the fact that a large proportion of the influent organic matter is usually in particulate form (> 40% in terms of COD, Marani et al., 2004) and is thus retained near the inlet by sedimentation and filtration (Langergraber et al., 2003). In addition, microbial biofilms proliferate and adhere to the granular medium at a higher rate near the inlet area in comparison with other locations, due to the availability of nutrients and organic matter. While biofilms are essential to the wastewater treatment process, their decay products (mainly cell walls) are highly resistant to biological transformation processes, which may account for a significant proportion of the non-biodegradable sediment (Speece et al., 1997).

A series of experiments were conducted to better understand the factors that influence the performance of shallow horizontal subsurface-flow constructed wetlands (García et al. 2004a, 2004b, 2005; Aguirre et al., 2005; Caselles-Osorio and García, 2006b). In a nine-month study, two experimental SSF CWs were evaluated to determine the impact of two organic substrates—glucose and starch—on COD and ammonium removal efficiency (Caselles-Osorio and García, 2006a). The results demonstrated that SSF CWs fed with an influent containing either glucose (considered a readily biodegradable compound), or starch (considered a slowly biodegradable compound), when operated at a somewhat low organic loading rate (6 g COD/m².day), yielded similar COD removal efficiencies, which ranged from 85 to 95% (\$\nabla > 0.05\$). These results were obtained under different hydraulic retention times (HRTs), both with and without sulphate in the influent.

The present study was conducted over a period of four months and constitutes a companion study to the one described above (Caselles-Osorio and García 2006a). Its objective was to evaluate the two experimental SSF CWs using a significantly higher organic loading rate (22 g COD/m².day vs 6.0 gCOD/m².day) than that used in the aforementioned study. Thus, this study was designed to determine the effects of a higher loading rate of the two substrates—glucose and starch—on the elimination efficiency of COD and ammonium. We assumed that the lack of differences between the glucose- and the starch-fed systems for COD removal in our previous study was perhaps due to the relatively low load used in the experiments. In this paper,

theoretical mass balance calculations were also undertaken to estimate the relative contributions of denitrification and sulphate reduction to organic matter oxidation.

3.3. MATERIAL AND METHODS

The two experimental SSF CWs used in this study were the same as those used in previous studies (Caselles-Osorio and García 2006a). The wetlands consisted in bottom flat plastic containers (0.93 m long, 0.59 m wide and 0.52 m high) filled with granitic gravel and with a drainage pipe located on the bottom of one of their sides. Gravel depth was 0.35 m (the diameter at which 60% of the material passed through the sieve was D_{60} = 3.5 mm, the uniformity coefficient was C_u = D_{60}/D_{10} = 1.7 and the initial porosity was 40%) and the water level was maintained at 0.05 m under the gravel surface to give a water depth of 0.30 m. In this study, the two SSF CWs were relocated to an outdoor terrace on the premises of our department building at the Technical University of Catalonia. The SSF CWs were replanted with common reed (*Phragmites australis*) rhizomes in January 2004 and experiments were conducted from February to May 2005. Although during the study a conspicuous plant cover was attained, the reed's stems were thinner and shorter than is usually observed in the field.

The experiment was conducted in a similar way to that described in the companion paper (Caselles-Osorio and García, 2006a). Every day, the two SSF CWs were batch loaded with 20 L of freshly prepared synthetic wastewater. The wastewater was added to the influent zone over a period of 20 minutes. The daily flow rate allowed to maintain a nominal HRT of 3 days. The two synthetic wastewater solutions were prepared by adding an organic substrate consisting of either 12 g of glucose (a dissolved compound, considered readily biodegradable) or 11.4 g of starch (a particulate compound, considered slowly biodegradable) to 20 L of tap water. These amounts of organic substrate ensured that the organic load was three times higher (approximately 18 gCOD/m².d) than that used in the companion study. Major nutrients were supplied by adding 3.0 g of NH₄Cl and 0.27 g of KH₂PO₄ to the influent. All these amounts were calculated to have a C:N:P ratio of approximately 100:16:1. The tap water used in this study is characterized by its high salinity (>1000 μ S/cm), high sulphate content (>150 mg/L) and very low levels of organic matter and major nutrients (AGBAR, 2004).

Throughout the experiment, influent, and effluent wastewater samples were collected at approximately weekly intervals. The effluent samples were obtained from the water volume displaced (stored in a vessel) when the influent was added to each SSF CW. The water samples were immediately analyzed for

temperature, turbidity, dissolved oxygen (DO), ammonium, nitrate, sulphate and COD. Temperature was measured using a Chektemp-1 Hanna thermometer, turbidity with a Hach 18900 turbidimeter, and the other parameters were analyzed using conventional methods described in APHA-AWWA-WPCF (2001). Potential evapotranspiration was estimated using the Thornthwaite equation (Martín, 1983). The climate data needed for the calculations were obtained from a nearby meteorological station. Analysis of variance (ANOVA) was used to test differences between the two SSF CWs with respect to contaminant removal efficiency. All of the variables were tested to ensure that they were normally distributed.

The mass balance concept of glucose equivalents (García et al., 2004a), was used to calculate the relative contribution of sulfate reduction and denitrification to removal of COD. The assumptions and stoichiometric relationships used in this study were identical to those discussed in Garcia et al. (2004a). The numerical differences between COD influent and effluent values were multiplied by 0.94 to convert the differences to glucose equivalents. For sulfate reduction, the difference in influent and effluent values was divided by 1.6 based on a sulfate to glucose mass ratio of 1.6. This is based on the following stoichiometric equation:

$$C_6H_{12}O_6 + 3SO_{4^-} \rightarrow H_2O + 3H_2S + 6H_2O$$

For organic matter removal via denitrification, it was assumed that 10% of the ammonium was removed by biological assimilation, and the rest was removed via the nitrification-denitrification pathway according to the following: The difference in influent and effluent ammonium concentrations was multiplied by 0.9 and that product was multiplied by 4.43 (see discussion below). This new product was then divided by 1.38 (see discussion below), to derive the appropriate glucose equivalent value. Thus, the nitrate to glucose stoichiometric relationship was based on the following equations:

$$NH_4^+ + 20_2 \rightarrow NO_3^- + H_2O + 2H_1^+$$

$$C_6H_{12}O_6 + 4NO_3$$
 $\rightarrow 6CO_2 + 6H_2O + 2N_2 + 4e^-$

in which the ammonium to nitrate ratio was 4.43 and the nitrate to glucose ratio was 1.38. Organic matter that was not removed via sulfate reduction and denitrification was assumed to have been removed via a combination of aerobic respiration and methanogenesis.

3.4. RESULTS AND DISCUSSION

Table 3.1 summarizes average values (and standard deviations) for effluent water temperature, turbidity, DO and potential evapotranspiration. Both temperature and DO concentration were similar for each of the SSF CWs throughout the study. Influent turbidity for the wetland fed with glucose was near zero, whereas it was higher for the system fed with starch (around 35 NTU) due to the particulate nature of the starch. During the initial weeks of the experiment, the values for effluent turbidity in the two wetlands were rather erratic and high, ranging approximately from 10 to 80 units (Figure 3.1). We surmise that initially, precipitates formed during our previous studies were resuspended when the 20 L of wastewater were poured on a daily basis into each SSF CW. It is also possible that the high organic loading rates and the ensuing reduced environment caused the precipitation of CaCO₃ and other carbonates, and the formation of elemental sulphur. In similar cases, carbonate precipitation and elemental sulphur formation are related to the presence of hydrogen sulphide and resulted in the water turning a characteristic off-white colour (Hammes and Verstraete, 2002). Although turbidity was rather high during the first 35 days of the experiment, from that time it decreased in both systems and stabilized at values of less than 5 NTU (Figure 3.1).

Influent DO concentrations were near saturation; however, effluent DO values were extremely low for both systems and in most cases concentrations were below the detection limit of the oxymeter. Such low effluent DO concentrations, coupled with high organic loading rates, are indicative of a strongly reducing environment suitable for denitrification, sulphate reduction, and methanogenesis.

Table 3.1 Averages and standard deviations (in brackets) of the effluent water temperature, turbidity, and DO in the experimental SSF fed with glucose and starch. Calculations were made using 30 data approximately. Potential evapotranspiration values were calculated with the Thornthwaite expression.

Temperature (°C) Turbidity (NTU)			DO (mg/L)				Evapotranspiration (mm/d)				
Glucose	Starch	Glu	icose	St	arch	Glu	cose	Starch		Glucose	Starch
Eff	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff	2.1	2.1
10.8	10.7	0.9	21.9	35.7	18.5	9.9	< 0.05	9.6	< 0.05	(0.6)	
(5.5)	(5.4)	(0.3)	(26.0)	(7.0)	(19.8)	(0.4)	(-)	(0.5)	(-)	(0.0)	(0.6)

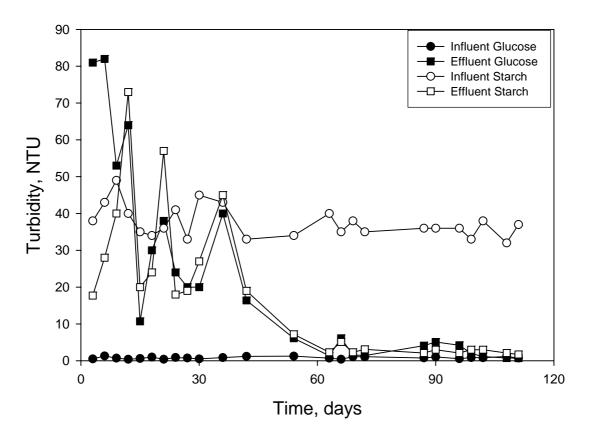


Figure 3.1 Temporal changes of turbidity in glucose and starch fed experimental SSF CW.

The influent COD concentration in the starch-fed SSF CW was slightly lower due to the inevitable settling and adsorption in the vessel used for the feeding process (Table 3.2). Despite the high organic loading rates, average COD removal in the two SSF CWs was near 90% (Table 3.2). COD removal was very stable in both systems, with very few temporal variations (Figure 3.2). As in the previous companion study, there were no significant differences between the experimental wetlands with respect to COD removal rates (p>0.05).

Table 3.2 Concentration averages (mg/L), standard deviations (in brackets) and mean removal efficiencies of the COD, ammonium and sulfates in the experimental SSF CW feed with glucose and starch. Calculations were made using 36 data for COD; 28 for ammonium and 33 for sulfate.

		Glucos	е	Starch			
Parameter (mg/L)	Influent	Effluent	Removal efficiency (%)	Influent	Effluent	Removal efficiency (%)	
COD	606 (26)	50 (19)	92	541 (67)	49 (13)	91	
NH_4 +- N	42 (3)	18 (7)	57	42 (4)	24 (10)	43	
NO ₃ -N	1.4 (0.13)	0.06 (0.23)	95	1.4 (0.13)	0.07 (0.16)	95	
SO ₄ ² -	130 (25)	8 (9)	93	130 (25)	17 (13)	87	

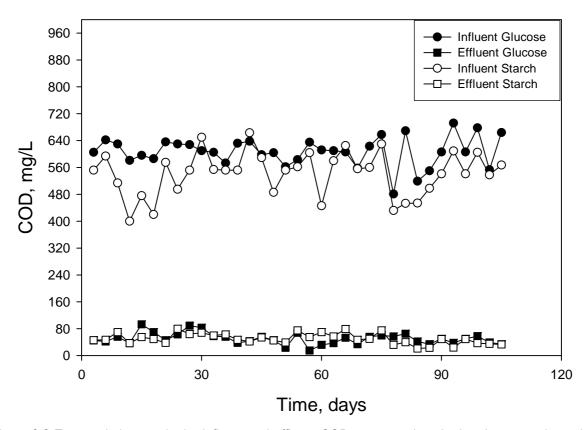


Figure 3.2 Temporal changes in the influent and effluent COD concentrations in the glucose and starch fed SSF CW.

The ammonium removal rates were significantly higher (p< 0.05) in the glucose-fed system than in the starch-fed system (Table 3.2). Influent and effluent nitrate concentrations were very low (< 0.5 mg NO₃-N/L), and were therefore not considered in any of the mass balance calculations. Effluent ammonium concentrations and removal dynamics varied considerably over time in the two SSF CWs (Figure 3.3). During the first week of the study, both systems had relatively high removal rates of ammonium (63-65%), but the removal rates became progressively lower over the next 30 days (42-51%). Over the last 45 days, ammonium removal rates improved (60-69%), and effluent concentrations were frequently below 10 mg/L. The higher ammonium removal rates observed in the glucose-fed system (both in this study and in the previous work, Caselles-Osorio and García, 2006a) may be related to the biodegradability properties of the glusoce versus the starch. It is reasonable to assume that in the system fed with glucose, which is a readily biodegradable compound, the heterotrophic microbial growth (microbial immobilization) would be more

intense than in the system fed with starch, which is a slowly biodegradable substrate (Mino et al., 1995). Differences in microbial growth would result in a greater ammonium assimilation (and therefore removal) in the glucose-fed wetland.

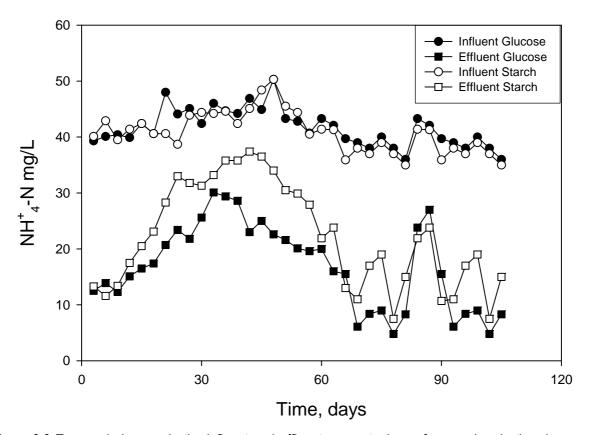


Figure 3.3 Temporal changes in the influent and effluent concentrations of ammonium in the glucose and starch fed SSF CW.

The sulphate concentration in the influent was quite high and variable, while the effluent concentrations were clearly lower (Table 3.2, Figure 3.4). During the first 30 days of the essay, sulphate concentrations in the effluent of the starch-fed system were higher than in the glucose-fed system. Nevertheless, these differences were transient and disappeared within 30 days. Beyond this time, both systems behaved similarly with respect to sulphate removal. We surmise that the early differences were due to the fact that glucose is more easily biodegradable and thus rapidly promoted greater rates of sulphate reduction. Despite the early differences metioned above, overall sulphate removal rates were very high in both systems, and there were

no significant statistical differences between them (p>0.05). In our previous study, in which the surface organic loading rates were one-third of the current rates, sulphate removal rates were lower than those observed in the present study and ranged from 66 to 75% (Caselles-Osorio and García, 2006a). Positive correlations between sulphate removal and surface organic loading rates have been pointed out in other studies (Aguirre et al., 2005; Weissner et al., 2005b; García et al., 2004a).

García et al. (2004a) provided background assumptions and stoichiometric relationships required for estimating the relative contribution of denitrification and sulphate reduction to the removal of organic matter. The calculated values were transformed into standardized glucose equivalents to facilitate comparisons within and between experiments. These standardized values have been calculated in the present study and are summarized in Table 3.3, as well as selected values from García et al. (2004a) and Caselles-Osorio and García (2006). The standardized glucose equivalent values for COD removal in the glucose- and starch-fed systems tested in the present study were much higher than those reported in the other studies by García et al. (2004a) and Caselles-Osorio and García (2006a). This was due primarily to the higher amounts of organic matter applied and removed in the two experimental systems (Table 3.3). In the present study and in our previous work with the same wetlands (Caselles-Osorio and García, 2006), the elimination of organic matter by means of denitrification represented a low amount in comparison to that reported for wetland D1 in the investigation of García et al. (2004a). This is related with the fact that D1 operated in general with a lower organic loading rate (4.0-11.8 g COD/m².d). On the other hand, in the present study, although sulphate removal was relatively high (averaging 87-93%) and therefore sulphate reduction activity was great, its contribution to organic matter removal only accounted for small portion (14-15%) of the overall removal of organic matter. In contrast, sulphate reduction accounted for 34 and 41% of the organic matter removed in the studies by Caselles-Osorio and García (2006), and García et al. (2004a), respectively. Note that the values of the "Residual" row in Table 3 were estimated by subtracting the percentage of glucose equivalent values for denitrification and sulphate reduction from the total glucose equivalents removed (the "COD" row). Therefore, the "Residual" values, which ranged from 72-73% in this study, represent the contributions of the other two major biochemical pathways: methanogenesis and aerobic respiration.

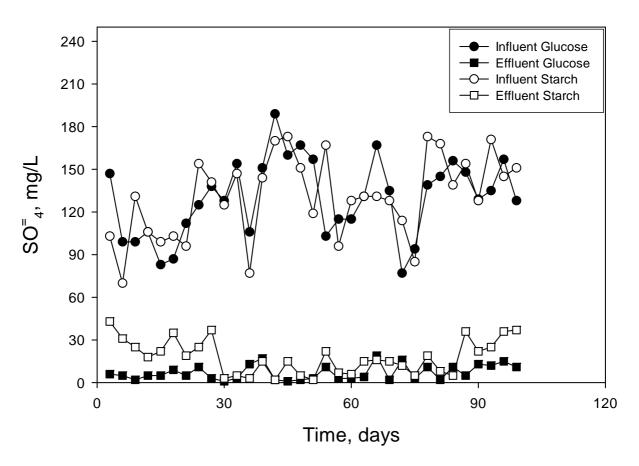


Figure 3.4 Temporal changes in the influent and effluent sulfate concentrations in the glucose and starch fed SSF CW.

We surmise that methanogenesis may have been a major pathway in the present study (highly loaded wetlands) based on the rapid depletion of dissolved oxygen (below detection limits in the effluent), and the high rates of sulphate reduction. The results of the present study coupled with those from previous investigations indicate that the organic loading rate has a major influence on the extent to which the different biochemical pathways contribute to organic matter degradation. However, it should also be noted that, this mass balance approach does not account for other significant removal mechanisms such as sedimentation, adsorption, volatilization, and microbial immobilization (Guellil et al., 2001; McCracken et al., 2002).

as GEs. In the column "GEs "" it is presented the percentage of glucose equivalents removed by sulphate reduction, denitrification and other pathways. The denitrification and SO42- through sulphate reduction) expressed as a percentage of the glucose equivalents (GEs removed). Data from the present study as Table 3.3. Average influent and effluent concentrations of wastewater constituents and estimates of their respective effect on organic matter (NH4+ through well from previous works for comparison are presented. Note that the organic matter removed values (in the "GE removed" column) have been standardized values indicated in the "residual" row represent the percentage of GEs not removed by denitrification and sulphate reduction, e.g., methanogenesis and aerobic respiration (other pathways).

		ž			_	_	
Na Ma		GEs %			53.1	<u>\$</u>	6.1
_		æ	removed	eg-	56	20	m
Starch		GE\$	36		8.7	33.6	57.7
		믮	removed	88	8.9	98	7.2
ilucose*		ű	žę		6.0	34.5	59.4
Ollo		띵	removed	127	42	=	1 8
rch	(fhis study)	GEs%			13	15.4	73.4
뫓	(this	믕	removed	462	S	7	339
ose	budy.)	GEs %			13.2	14.5	72.3
Ollic	(this study)	w	removed	l	8		378
		å		88-38	27.4.18.5	72-40	
values		Starch		145.47	13.8,2	168-82	
uent average	(mg/L)	Glucose		168-41	13.8.8	168-57	
Influent – Eff		Starch	(this study)	541-49	45.54	130-17	
		Glucose	(this study)	606-50	42.18	130-8	
Parameter				COD	N. THN	204	Residual

From Garcia et al. (2004a). Wetland D1 had a surface area of 55 m² and an average unater depth of 0.27 m. Its average organic loading rate ranged form 4.0 g CODAm² day From Caselles-Osorio and García (2006), in which the same experimental SSF CW used in the present study were tested but with an average load of 6.0 g CODAM: day

3.5. CONCLUSIONS

After approximately one year in operation, including the nine months of the companion study (Caselles-Osorio and García, 2006a) and four months of the present study, the two SSF CWs yielded excellent removal rates of COD under a wide range of operating conditions. In fact, the overall COD removal rates for glucose-and starch-fed systems were very similar (no statistical differences), ranging from 85 to 95%. Considering that the loading rates were much higher (20-22 g COD/m².d) in this study than in the companion study (6 g COD/m².d), there were few differences between the two studies. Thus, it is clear from these results that the organic matter removal efficiency of SSF CWs is not sensitive to the type of organic matter with which they are fed (whether dissolved or particulated) under a wide range of loads.

Mass balance calculations based on stoichiometric relationships indicated that in the highly loaded systems used in this study, denitrification and sulphate reduction were minor pathways for the removal of organic matter in comparison to other pathways. Indirect observations, such as a lack of oxygen in the effluent and the complete removal of sulphate, suggest that methanogenesis made a highly significant contribution to our experiments. These results contrast with those obtained in previous studies with lightly loaded SSF CWs, in which sulphate reduction and denitrification were major pathways. Other physico-chemical pathways such are sedimentation and adsorption can also have had a great importance in the present study.

The removal of ammonium was higher in the glucose-fed system (57%) than in the starch-fed system (43%) and statistically different. This trend had already been observed in our previous companion study and is attributed to the greater heterotrophic microbial growth in the glucose-fed system.

CHAPTER 4 EFFECT OF PHYSICO-CHEMICAL PRETREATMENT ON THE REMOVAL EFFICIENCY OF HORIZONTAL SUBSURFACE-FLOW **CONSTRUCTED WETLANDS***

Caselles-Osorio, A. and García, J. 2006. Effect of physico-chemical pretreatment on the removal efficiency of horizontal subsurface-flow constructed wetlands. Environmental Pollution. In press.

^{*} An early version of this chapter was published as:

4.1. ABSTRACT

In this study we tested the effect of a physico-chemical pretreatment on contaminant removal efficiency in two experimental horizontal subsurface-flow constructed wetlands (SSF CWs). One SSF CW was fed with settled urban wastewater, whereas the other with the same wastewater after it had undergone a physico-chemical pretreatment. The SSF CWs were operated with 3 different hydraulic retention times. During the experiments the effluent concentrations of COD, ammonium N and sulfate were very similar, and therefore the physico-chemical pretreatment did not improve the quality of the effluents. COD removal efficiency (as percentage or mass surface removal rate) was slightly greater in the SSF CW fed with pretreated wastewater. Ammonium N removal efficiency was, in general, similar in both SSF CWs and very high (80 to 90%). At the end of the experiments it was observed that in the SSF CW fed with settled wastewater the hydraulic conductivity decreased by a 20%.

4.2. INTRODUCTION

The increasing application of subsurface-flow constructed wetlands (SSF CWs) for the sanitation of urban wastewaters has proven their feasibility for removing organic matter, nitrogen and other contaminants. Several reports dealing with the performance of full-scale systems in different regions or countries have detected more or less the same advantages and disadvantages (Kadlec et al., 2000; Vymazal, 2002; Manios et al., 2003; Rousseau et al., 2005). The worst problem described by these studies is the progressive clogging that occurs near the inlet, which is a result of solids entrapment and sedimentation, biofilm growth, and chemical precipitation (Blazejewski and Murat-Blazejewska, 1997; Langergraber et al., 2003; Tanner et al., 1995, 1998). All of these processes promote the occlusion of interstitial spaces, which leads to a decrease in the hydraulic conductivity and effective volume, and an increase in the water velocity (Tanner and Sukias, 1995). In fact, surveys carried out on full-scale systems that have been in operation for several years have detected a 25% reduction in the initial volume of the SSF CWs (Kadlec and Watson, 1993; Dahab and Surampalli, 2001). To prevent the granular medium from becoming clogged very rapidly, Platzer and Mauch (1997) and USEPA (2000) recommend not to exceed an organic load of 25 g BOD/m².d in the case of vertical SSF CWs. In comparison, for horizontal SSF CWs is recommended an organic load lower than 6 g BOD/m².d (USEPA, 2000; García et al., 2005).

One possible way to reduce the clogging rate of an SSF CW is to use intensive preliminary processes such as coagulation and flocculation followed by clarification, membrane filtration and primary effluent filtration (Tchobanoglous et al., 2003). In turn, they could improve the removal efficiency of the SSF CWs, although there is no experimental evidence of this. Coagulation and flocculation have been widely used in wastewater treatment and, when combined with solids-separation units, are known as physico-chemical treatment. This treatment allows the removal of 80-90% of the suspended solids and 40-70% of the BOD (Metcalf & Eddy, 2003). Recent studies have shown the advantages of the use of a physico-chemical pretreatment for the removal of P in SSF CWs (Meers et al., 2006). The disadvantages of physico-chemical treatment include the cost of the coagulants, energy for mixing and adding the coagulants, possible changes in pH and alkalinity after the addition of the coagulants, and more sludge (Ødegaard, 1998). Furthermore, in remote locations where the maintenance can only be carried out infrequently the physico-chemical treatment may not be feasible.

The objective of this study was to evaluate the effect of a physico-chemical pretreatment on the effluent quality of SSF CWs. Two experimental SSF CWs were fed with wastewater from the same origin that had undergone different preliminary treatments. One SSF CW was fed with primary effluent (PE) and the other with physico-chemically pretreated primary effluent (PTPE). The efficiency of the systems was tested under different conditions. At the end of the experiments, the hydraulic conductivity was measured to determine how the physico-chemical treatment helped to maintain it.

4.3. MATERIAL AND METHODS

Experimental SSF CWs

The two SSF CWs consisted of PVC containers (0.93 m long, 0.59 m wide and 0.52 m deep) filled with gravel extracted from near the outlet of one bed of a pilot SSF CW system located in Les Franqueses del Vallès, Barcelona, Spain. A description of the pilot SSF CW can be found elsewhere (García et al., 2004a). Each container had a drainage pipe located on the bottom of the effluent side. The bottom was flat. The gravel layer was 0.4 m deep (D₆₀ =3.5 mm, C_u=1.7, and with an initial porosity of 40%) and the water level was kept 0.05 m under the gravel surface to give a water depth of 0.35 m (Figure 4.1). The experimental SSF CWs were planted in June 2004 with developed rhizomes of common reed (Phragmites australis) and placed on the roof of the Department of Hydraulic, Maritime and Environmental Engineering (Technical University of

Catalonia, Barcelona, Spain). By July 2004 the plants had established themselves and by September 2004 they covered the entire surface of the beds.



Figure 4.1 Experimental SSF CW fed with municipal wastewater with- or without a physico-chemical pretreatment. The experimental untits were located on the terrace of the Marine and Environmental Engineering Building of the UPC.

Influents and feeding strategies

Both SSF CWs were fed daily in batch mode with urban wastewater obtained from a municipal sewer located near the Department. One SSF CW was fed with primary settled wastewater (known as PE), and the other with the same settled wastewater (known as PTPE), after it had undergone a physico-chemical pretreatment (1 min of coagulation at 200 rpm, 15 min of flocculation at 20 rpm and 30 min of clarification; coagulant: 70 mg/L of Tanfloc-SG, Tanac, Brazil). The coagulant used is a non-toxic organic cationic polymer of low molecular weight that is completely biodegradable. Adding this coagulant to water does not change the alkalinity or pH. The physico-chemical treatment was performed using a standard jar-test device (Flocumatic P, Selecta). The experiments were carried out during three periods (from August to September 2004, from October 2004 to January 2005, and from February to March 2005), in which different operational conditions were applied to each SSF CW (Table 4.1). Both SSF CWs were fed in batch form during all the study by pouring the wastewater into one side of the system for 20 min. This feeding strategy was used instead of continuous operation in order to avoid solids sedimentation and adsorption onto the walls of tanks and pipes. Batch operation therefore made possible a good comparison of the performance of the 2 experimental SSF CWs. After adding the wastewater, it was discharged the same amount less the evapotranspiration (which was taken into account for calculating the mass removal rates). Throughout the study, two to three influent

and effluent grab samples were taken weekly and analyzed for electrical conductivity, turbidity, COD, ammonium N and sulfate using the methods described in APHA-AWWA-WPCF (2001). Temperature was measured with a Chectemp-1 Hanna thermometer, turbidity with a Hach 18900 turbidimeter, and electrical conductivity with an YSI 30 conductivimeter. Effluent samples were obtained from the water volume displaced when the influent was added (which was stored in a vessel). The performance of the SSF CWs was evaluated based on COD and ammonium nitrogen removal efficiency. Potential evapotranspiration was estimated using the Thornthwaite equation (Martín, 1983). The climate data needed for the calculations were obtained from a nearby meteorological station.

Table 4.1 Operational conditions used for the two SSF CWs in the three different experimental periods. The SD of the averages is shown in brackets. One SSF CW was fed with primary settled wastewater (PE) while the other was fed with the same wastewater after it had undergone a physico-chemical pretreatment (PTPE).

Period	,	st	2	nd	3	3 rd
Months	Aug-S	Sep 04	Oct 04	-Jan 05	Feb-N	Mar 05
Water used as influent Hydraulic loading rate (HLR), m³/m².d	PE 0.018	PTPE 0.018	PE 0.037	PTPE 0.037	PE 0.055	PTPE 0.055
Nominal hydraulic retention time (HRT), d	6	6	3	3	2	2
Applied organic surface loading rate, g COD/m ² .d	6	3	14	7	20	11
	(2.0)	(8.0)	(3.4)	(2.0)	(5.7)	(5.1)

The statistical procedures were carried out using the SYSTAT statistical software package. All of the relevant variables were tested to ensure that they were normally distributed. One- and two-way ANOVA procedures were used to evaluate the effect of physico-chemical pretreatment and the hydraulic retention time (HRT) on COD, NH₄+-N and SO₄²- effluent concentrations and mass surface removal rates of these substances.

Hydraulic conductivity tests (HCTs)

At the end of the experiments, HCTs were carried out near the inlet of each SSF CW (in exactly the same position) in order to examine the effect of the pretreatment on the hydraulic conductivity of the granular medium. Note that most of the SS are retained near the inlet and in this location is where the greater reduction in porosity occurs (Tanner et al., 1998). We used the method described in NAVFAC (1986) as the falling-head test. This is, in fact, a Lefranc test (which is commonly used in geotechnical studies) with variable water level. The HCTs were performed using a plastic tube 0.48 m long and 0.2 m in internal diameter, which was inserted vertically 0.2 m into the gravel. During the tests 5 to 6 L of tap water were added inside the tube in a pulse and the variation of pressure was monitored with a Druck PTX 630-1525 probe connected to a

computer by means of a Datataker DT50. The probe was placed inside the tube on the gravel surface and therefore the changes in pressure were proportional to changes of the water-column inside the tube. Measurements were obtained every second. There was still water in the SSF CWs when the tests were performed. The hydraulic conductivity was estimated using the equation described in NAVFAC (1986), which is obtained by combining the mass conservation principle and Darcy's law:

$$K = \frac{d^2 \ln(2L/d)}{8Lt} \ln \frac{h_1}{h_2}$$

where:

K is the hydraulic conductivity, in m/s h_1 is the initial water height inside the tube, in m h_2 is the water height inside the tube at time t, in m d is the internal diameter of the tube, 0.2 m L is the length of the tube that is submerged, 0.2 m t is the time, in s

In order to estimate hydraulic conductivity, an iterative procedure was used in conjunction with least-squares fitting. Residuals were obtained from the difference between the theoretical h₂ values and the field data. Note that the hydraulic conductivity found with this method is in fact "apparent" and therefore the values obtained cannot be compared with others from different systems. Probably, this is due to the small size of the experimental SSF CWs, which caused the water level to rise during the tests somewhat instead of allowing complete horizontal displacement.

4.4. RESULTS AND DISCUSSION

The average water temperature, turbidity, electrical conductivity and potential evapotranspiration for the two experimental SSF CWs are summarized in Table 4.2. Water temperatures were similar in the effluents of the two SSF CWs in all periods. The lowest temperature values were observed in the third period. The physicochemical treatment clearly reduced the turbidity of the influent. During the second period, both effluents were very clear and had low turbidity (which was also the case in most of the first period, although unfortunately no turbidity measurements are available). During the third period, when hydraulic loading rate was greatest (2 day HRT), the turbidity increased in both wetlands, especially in the PE SSF CW (Figure 4.2). The high turbidity values seem to be due two factors that may occur at the same time: the precipitation of CaCO₃ and

other carbonate salts, and the formation of elemental sulfur from the oxidation of H₂S that gave the water a characteristic white-grey color. Carbonate precipitation and sulfur formation in anaerobic environments is related to the presence of hydrogen sulfide, which is released through the activity of sulfate-reducing bacteria (Hammes and Verstraete, 2002). Thus, the increase in the organic surface loading rate in both experimental SSF CWs in the third period probably promoted the sulfate-reduction reaction, which in turn released enough hydrogen sulfide to cause carbonate precipitation and sulfur formation. This statement is supported by the higher sulfate removal observed in the third period (see Table 4.3). Also note that, in the third period, the turbidity peaks that appeared between days 170 and 180 were due to dark-colored precipitates that were probably formed by the reaction of hydrogen sulfide with metals such as iron (Wright, 1999). The high metal concentrations may have been related to uncontrolled discharges to the municipal sewer. Dark-colored precipitates were probably washed out from the SSF CWs in relation with the batch-feeding strategy (30 L in 20 min). In continuously fed systems these precipitates would remain deposited unless the flow rate was too high.

Table 4.2 Averages and SD (in brackets) of the water temperature, turbidity, electrical conductivity and potential evapotranspiration of experimental SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical pretreatment (PTPE) in the various periods. Calculations were carried out using 30 data in first period, 60 in the second and 30 in the third. "nm" means "not measured". Evapotranspiration values were calculated with the Thornthwaite expression.

Period	,	erature C)	Turbidity (NTU)			Electrical conductivity (µS/cm)			/ity	Evapotranspiration (mm/d)		
	PE	PTPE	Р	E .	PT	PE	PE PTPE		PE	PE	PTPE	
-	Eff	Eff	Inf	Eff	Inf	Eff	Inf	Eff	Inf	Eff		
1st	24	24	nm	nm nm	nm	nm nm	2000	2000	2000	2100	3.8	3.8
	(1.4)	(1.4)	nm	nm	Ш		(530)	(280)	(540)	(280)	(8.0)	(8.0)
2^{nd}	17	16	115	1.4	20	1.7	2900	2800	2200	2900	1.2	1.2
	(4.6)	(5.0)	(77)	(0.4)	(13)	(1.7)	(420)	(360)	(340)	(420)	(0.7)	(0.7)
3^{rd}	13	12	120	44	20	34	2000	2200	2000	2500	2.9	2.9
	(3.5)	(3.5)	(46)	(26)	(14)	(43)	(420)	(430)	(410)	(570)	(1.2)	(1.2)

In general, electrical conductivity was slightly higher in the effluents than in the influents, probably due to plant evapotranspiration (Table 4.2). Note that the coagulant used in the physico-chemical treatment reduced the electrical conductivity of the settled wastewater in the second period. This capacity is specified by the manufacturer. It is not known why the electrical conductivity was reduced in the second period and not in the others.

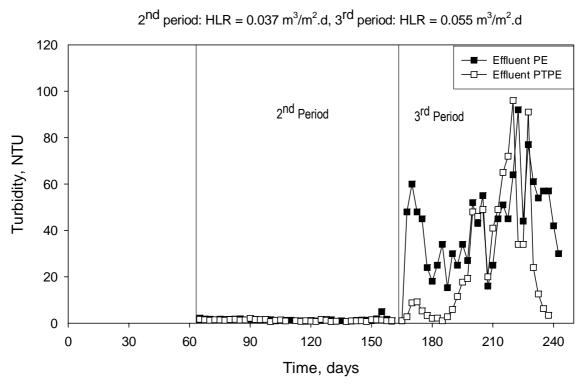


Figure 4.2 Changes over time of the effluent turbidity in the SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical treatment (PTPE). Only measurements from the second and the third period are available.

The changes over time of COD concentrations in the influent and the effluent are shown in Figure 4.3. The influent COD concentration was lower in the SSF CW fed with PTPE due to the physico-chemical treatment, which reduced the COD concentration approximately by half (Table 4.3). The concentration of COD in the effluent PTPE was slightly smaller than in effluent PE, especially in the last period, when the surface loading rate was the highest in both SSF. The COD mass surface removal rate was clearly higher in the SSF CW fed with PE (Table 4.4). Global effluent COD concentration differences between the two SSF CWs were statistically significant (Table 4.5). Although the COD effluent concentrations were not significantly different in the first period, the global results allow us to conclude that the physico-chemical pretreatment slightly improved the quality of the effluents. On the other hand, COD percentage removal efficiencies and the COD mass surface removal rates were higher in the PE SSF CW due to the greater influent COD concentration. This trend shows that the efficiency of SSF CW systems cannot be evaluated using just the removal

percentage or the mass surface removal rate, because mainly depend on the influent properties and not on the effluent quality. The fact that removal efficiency (in terms of percentage or mass surface rate) increases with increasing inflow concentration is well known.

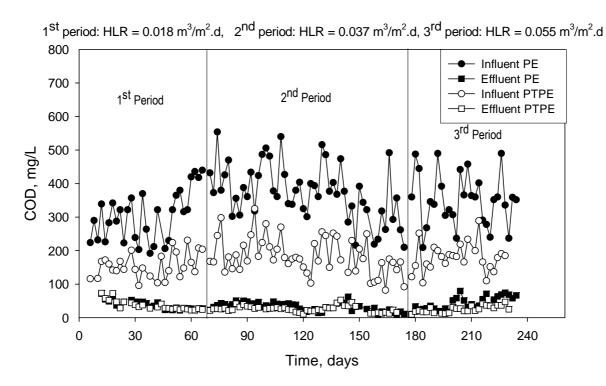


Figure 4.3 Changes over time of the influent and effluent COD concentration in the SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical treatment (PTPE).

Several studies have pointed this out and have suggested that only systems that treat influents with similar contaminant loads can be reasonably compared (Schierup et al., 1990; Tanner et al., 2002; Headley et al., 2005; Kadlec et al., 2005).

Table 4.3. Concentration averages, SD (in brackets) and mean removal efficiencies (Rem) of the COD, ammonium N and sulfates in the experimental SSF CWs fed with primary settled wastewater (PTPE) in the same wastewater after it had undergone a physico-chemical treatment (PTPE) in the various periods. Calculations were carried out using 30 samples in the first period, 58 in the second and 29 in the third.

	Rem	æ		<u>1</u> 2		귝		24	
PTPE	#	\$0 7	(mg/L)	138	24	35	6	135	8
	Ψ	\$0 7	(mg/L)	28	2	亞	83	38	8
	Rem	8		12		~		Ø	
F	25	\$0°	(mg/L)	1	62	155	69	3	8
	Ψ	\$0°	(mg/L)	181	€	沒	(34)	167	6
	Rem	8		e		븅		Œ	
PTPE	击	곡 포	(mg/L)	20	8	- 2	€	€	æ
	重	곡 포	(mg/L)	z	8	83	E	æ	ē
	Rem	Z		84		9		65	
PE	击	<u>국</u> 포	(mg/L)	3.4	Ø	5.6	Q	ę	G
	型	<u> </u>	(mg/L)	23	න	35	E	37	@
	Rem	æ		92		æ		8	
PTPE	#	8	(mg/L)	£	3	32,	න	23	Ð
	¥	80	(mg/L)	156	9	\$	9	9	€
	Rem	8		88		동		83	
밆	#	80	(mg/L)	#	E	33,	22	4	8
	型	80	(mg/L)	322	£	88.	3	38	(E)
Period				tK.		54		æ	

Table 4.4 Averages and SD (in brackets) of the mass surface removal rates of COD, ammonium-N and sulfates in the experimental SSF CW fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical pretreatment (PTPE) in the various periods.

Period —	COD, g	COD, g/m ² .d)		n N, g N/m².d	Sulfate, g/m².d		
	PE	PTPE	PE	PTPE	PE	PTPE	
1 st	5.3 (2.1)	2.2 (0.8)	0.4 (0.2)	0.35 (0.2)	0.35 (0.2)	0.48 (0.3)	
2 nd	12.8 (4.7)	5.8 (2.0)	1.2 (0.5)	1.1 (0.5)	0.4 (0.3)	0.25 (0.1)	
3rd	17.5 (6.3)	9.6 (4.0)	1.3 (0.5)	1.2 (0.4)	2.0 (1.4)	2.2 (1.3)	

The ANOVA test showed that the HRT significantly affected the effluent COD concentrations and also the COD mass surface removal rates (Table 4.5). However, the results did not show a clear pattern between HRT and effluent COD because the concentration values were lower in the second period than in the others. The mass surface removal rates increased with lowering the HRT. Lack of clear relationship between HRT and effluent COD concentration may be related to weather conditions since the tests were performed in different periods. In the third period, the fact that the average effluent COD in the PE SSF CW was higher than in the other periods could be due to solids washout in relation to the greater flow rate. It is possible that in this period some water may have passed directly through the bed to the outlet during the feeding the system. In the PTPE SSF CW, the average effluent COD concentration was very similar in the second and third periods. This trend seems to be the reason for the significant interaction between HRT and wastewater type.

Table 4.5 Probabilities of the ANOVA test on the effects of the factors (one-way) and their interaction (two-way) on the mass surface removal rates and effluent concentrations of COD, ammonium N and sulfates. Nomber of samples: n = 202 for COD; n = 220 for NH₄+-N and n = 164 for SO₄²-.

Variable tested	Type of influent wastewater	HRT	Type of influent wastewater*HRT
COD mass surface removal rate	0,000a	0,000a	0,000a
COD effluent concentration	0.000a	0.003a	0.010a
Ammonium N mass surface removal rate	0.066	0.000 a	0.689
Ammonium N effluent concentration	0.933	0.000a	0.043a
Sulfate mass surface removal rate	0.560	0.000 a	0.862
Sulfate effluent concentration	0.748	0.032a	0.243

^a Statistically significant differences at a significance level of 0.05.

The changes over time of ammonium N concentrations in the influent and effluent of the two SSF CWs are shown in Figure 4.4. The effluent ammonium N concentrations, percentage removal efficiencies, and mass surface removal rates within a HRT were similar in the two SSF CWs in the different periods (Tables 4.3, 4.4).

and 4.5). The ANOVA test indicates that HRT significantly affected both ammonium N effluent concentrations and mass surface removal rates. Figure 4.4 clearly illustrates that the effluent concentrations were higher in both SSF CW in the third period (with the lowest HRT). With respect to the mass surface removal rates of ammonium N, it is apparent that as the HLR increased from first to the second period, there was a concomitant increase in mass removal rates. However, when the HLR increased from the second to the third period, the ammonium N mass surface removal rates were very similar. It may happen than in the third period the HRT was too short for producing effluents with a low ammonium N concentration as occurred during the previous periods.

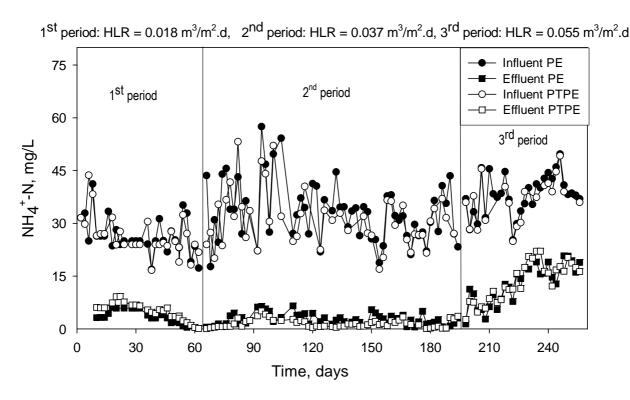


Figure 4.4 Changes over time of the influent and effluent ammonium N concentration in the SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical treatment (PTPE).

The results of the present study show that both experimental SSF CWs had excellent ammonium N removal efficiency, especially at a HRT of 6 and 3 days, when removal percentages ranged from 80-90%. Several different studies have been conducted in horizontal SSF CWs having a similar water depth and the removal percentages were around 50% (Neralla et al., 2000; García et al., 2004a; Kaseva, 2004; Aguirre et al., 2005). The main mechanism for ammonium N removal in SSF CWs that treat urban wastewater is normally the nitrification reaction, which is favored by the oxygen transported by the aerial parts of the plants towards the rhizosphere and by the surface reaeration of the bulk water (Brix, 1990; Tanner, 2001; Tanner and Kadlec, 2003). These two processes are enhanced as the water depth decreases (Aguirre et al., 2005; García et al., 2005). García et al. (2005) have proven that the bulk water in shallow beds (0.3 m) is in more oxidized conditions than in deep ones (0.5 m) when the same wastewater is treated with the same surface organic loading rate. Therefore, the shallowness of the experimental SSF CWs tested in this study may help to explain their high ammonium N removal efficiencies. Furthermore, these high efficiencies could also be linked to the batch-feeding strategy. Stein and Kakizawa (2005) have observed that experimental systems fed in batch mode removed ammonium N more efficiently (44%) than those fed with continuous flow (38%). The greater efficiency of batch-loaded systems was related to better oxidizing conditions, which in turn favored aerobic processes such a nitrification (Stein et al., 2003). Lower ammonium removal efficiencies in the work of Stein and Kakizawa (2005) than in the present work could be due to differences in configuration of the systems tested (i.e. water depth).

The changes over time of the sulfate concentrations in the influent and effluent are shown in Figure 4.5. In general sulfate removal was rather low (in terms of percentage or mass surface removal rate), with the exception of the third period when the organic surface loading was the greatest (Tables 4.3, 4.4 and 4.5). The positive relationship between sulfate removal and organic surface loading rate has also been observed in previous studies (Aguirre et al., 2005; García et al., 2004a). In these studies, the average percentage sulfate removal was higher that in the present investigation (normally over 40%) and depended on the water depth.

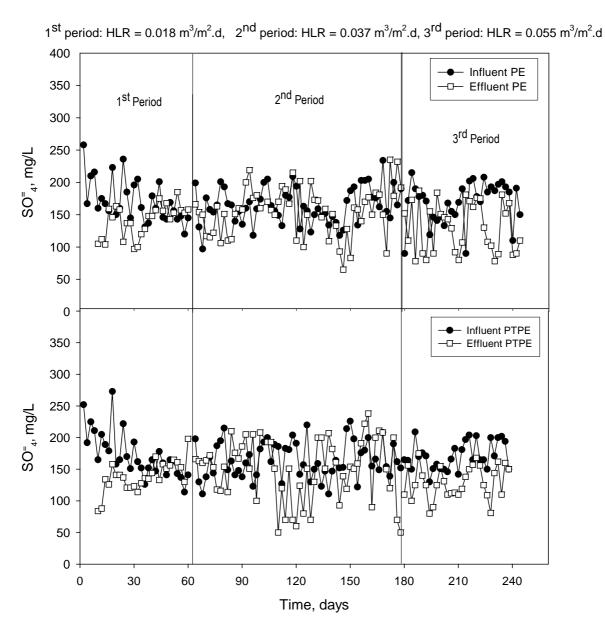


Figure 4.5 Changes over time of the influent and effluent sulfate concentrations in the SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical treatment (PTPE).

Figure 4.6 shows the changes over time of the water level inside the tubes used for the HCTs performed near the inlet of the two experimental SSF CWs. The water height in the SSF CW fed with PE decreased more slowly, which indicates lower hydraulic conductivity. Accordingly, the estimated hydraulic conductivity value was slightly higher in the PTPE (25 m/d) than in the PE (20 m/d). These "apparent" values are in fact somewhat lower than the actual hydraulic conductivity because of the small size of the SSF CW; however, they can be compared. These results indicate that the larger amount of influent particles retained near the

inlet in the SSF CW fed with PE tends to cause the hydraulic conductivity to decrease more. Therefore, it seems that the physico-chemical treatment had a positive effect on maintaining higher hydraulic conductivity.

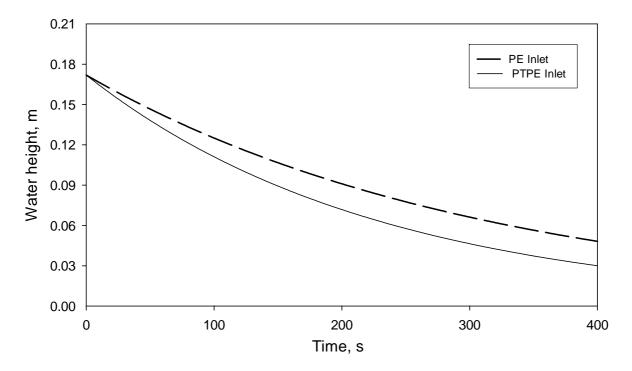


Figure 4.6 Changes over time of the water level inside the tubes during the HCTs performed near the inlet of the SSF CWs fed with primary settled wastewater (PE) and with the same wastewater after it had undergone a physico-chemical treatment (PTPE).

Watson and Choate (2001) estimated hydraulic conductivity values of 900 and 12000 m/d for the inlet and outlet zones respectively in a long, narrow SSF CW that had been operating for more than 10 years. Therefore, by comparing these two values, hydraulic conductivity decreased by more than 90% near the inlet. In our systems, the hydraulic conductivity in the SSF CW fed with PE decreased by 20%, but over the course of 8 months.

The model described in Zhao et al. (2004) has been used to estimate the time in which the experimental SSF CW will become clogged near the inlet. This model considers the available void space inside a bed at the start time of the operation (t=0) as $V_0 = \epsilon \cdot h \cdot A$, where ϵ , h and A represent average porosity (40%), depth of filtration layer (height of gravel, cm) and bed surface area (cm²) respectively. As the bed operates, V_0 is gradually congested by the suspended solids (SS) and the available void space after " t_c " days operation is thus reduced (V_{01}). To calculate the occupied volume during t days' operation, the model considers the flow rate (L/d), the

concentrations of SS (mg/L) in the influent and effluent, density (mg/cm³) and moisture content (%) of SS. Therefore, clogging time can be predicted as:

$$t_{c} = \frac{V_{01}\rho_{s}(1-MC)}{Q(C_{1}-C_{2})}$$

where:

t_c is the clogging time, in d

V₀₁ is the available void space in filtration/clogging layer after operation time, in cm³

 ρ_s is the density of SS, mg/cm³

MC is the moisture content, %

Q is the flow rate, L/d

C₁ is the concentration of SS in the influent, mg/L

C2 is the concentration of SS in the effluent, mg/L

For calculations it was considered that SS concentration was a 22% of the total COD in the SSF CW fed with PE (this value has been obtained from a previous work with a large data set in which the same wastewater was used (Barajas et al., 2002)). In addition, it was assumed that the physico-chemical pretreatment removed 85% of the SS (Metcalf & Eddy, 2003). The values of density (1050 mg/cm³), moisture content (94%), fraction of organic matter (80%) and fraction of biodegradable organic matter (90%) of SS were obtained from Blazejewski and Murat-Blazejewska (1997). Note that for calculations it was considered the recovery of the void space due to the biodegradation of the accumulated solids. According to this model, the SSF CWs fed with PE and that fed with PTPE needed 547 and 4024 days respectively to become completely clogged. From these results it is clear that the SSF CW fed with PE is more susceptible to clogging processes, and the physicho-chemical pretreatment allows to expand the life-span of the SSF CW in approximately 10 years. However, these results are only indicative because this model does not take into account biofilm growth and the influence of vegetation and its contribution to the increase of recalcitrant detritus.

On the other hand, Rousseau (2005) developed a mechanistic model that estimates reductions in pore volume in SSF CW as a function of time. This model was used by García et al., 2006 to estimate the reduction in pore volume and the subsequent loss of porosity in an experimental SSF CW related to the present work. The hypothesis being tested was that pretreatment of the influent wastewater with a physico-chemical

treatment could reduce the risk of clogging and loss of porosity. In fact, after 120 days of operation in some regions of the SSF that were fed with primary setteable influent wastewater, the porosity was diminished by 17%. However, in the SSF fed with the same setteable wastewater but with a physico-chemical pretreatment, porosity was diminished by only 6%.

The values of the COD removal first-order volumetric constant rates (k_{v,20}) are shown in Table 4.6 for both experimental SSF CWs and for the three HRT's. To calculate the rates, it was assumed that the SSF CWs behaved like plug-flow reactors with axial dispersion under open-open boundary conditions (García et al., 2004b). The dispersion number values were obtained from another previous study in which a nonreactive pharmaceutical product (clofibric acid, used as a tracer) was injected to both experimental SSF CWs (Matamoros et al., unpublished data). The values of the first-order rate were calculated using an iterative procedure for solving the following equation (Crites and Tchobanoglous, 1998):

$$\frac{C_2}{C_1} = \frac{4 \cdot a \cdot e^{(\frac{1}{2}D)}}{(1+a)^2 e^{(\frac{a}{2}D)} - (1-a)^2 e^{(-\frac{a}{2}D)}}$$

Where.

C₁ is the influent COD concentration, mg/L

C2 is the effluent COD concentration, mg/L

a is
$$\sqrt{1 + 4 \, k_{v,20} \, t \, D}$$

D is the dispersion number, 0.035 for both SSF CWs

k_{v,20} is the first-order volumetric kinetic constant at 20 °C, d-1

t is the hydraulic retention time, d

Table 4.6 Values of the COD removal first-order volumetric constant rates at 20 $^{\circ}$ C ($k_{v,20}$, d^{-1}) for both experimental SSF CWs and in the different periods.

Period	PE	PTPE
1 st	0.42	0.29
2 nd	1.23	0.82
3 rd	1.14	0.86

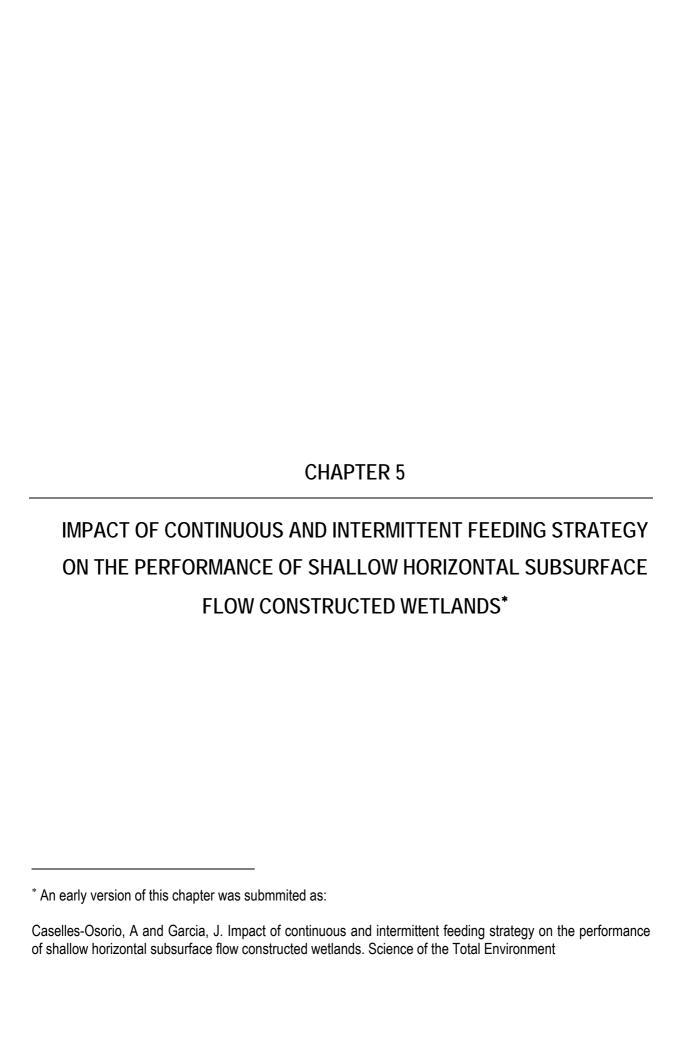
Average influent and effluent concentrations COD obtained in each of the three periods were used for the calculations. The rates were corrected for temperature using the Arrhenius equation with an adimensional temperature coefficient of 1.04 (Crites and Tchobanoglous, 1998). The $k_{v,20}$ values were lower in the SSF CW fed with PTPE than in the SSF CW fed with PE, according to their different removal efficiencies (Tables 4.3 and 4.4). In fact, the $k_{v,20}$ values were positively related to the COD influent concentration. All of these values fit well in the range of magnitude found in the previous studies reviewed by Rousseau et al. (2004a). Note that from the data, first order areal-based kinetic constants ($k_{A,20}$) can be calculated considering the water depth (h) and the porosity (ϵ): $k_{A,20} = \epsilon \cdot h \cdot k_{V,20}$.

4.5. CONCLUSIONS

The use of a physico-chemical treatment as a preliminary step for SSF CWs did not clearly improve the quality of the effluents in terms of turbidity, COD and ammonium N, at least during the initial 8 months of operation. For COD concentrations, the greatest difference between the effluents of the two tested SSF CWs was observed when the HRT was the lowest (2 days, third period). In this case, the average COD level was 27 mg/L for the SSF CW fed with physico-chemically treated wastewater, and 44 mg/L for the SSF CW that received settled wastewater. The COD mass surface removal rate increased with the lowering of the HRT. It was observed that COD removal in terms of concentration (percentage of removal efficiency) was not dependent on the HRT (which ranged from 2 to 6 days), whereas ammonium N removal in terms of concentration clearly decreased in the third period (when the HRT was the lowest). The percentage of ammonium N removal ranged in most cases from 80 to 90%.

After 8 months of operation the SSF CW fed with settled wastewater had a lower hydraulic conductivity than the SSF CW fed with physico-chemically treated wastewater. In addition, it was estimated that the physico-chemical pretreatment allowed to extend the life-span of the SSF in approximately 10 years in comparison to the SSF fed with settled wastewater.

The physico-chemical treatment has certain requirements that can make this process unsuitable in the context of constructed wetlands technology: the costs of the coagulants, energy for adding and mixing coagulants, and more sludge handling. Thus, in each particular project should be evaluated whether the costs of the physico-chemical treatment compensate for the cost of replacing the medium after it becomes clogged. For wastewaters that contain an extreme COD concentration in the form of particles (for example, wastewaters produced during composting), it is clear that a physico-chemical pretreatment can significantly extend the lifespan of the SSF CWs and at the same time be economically viable. One another possible advantage of the physico-chemical pretreatment could be the additional removal of phosphorus.



5.1. ABSTRACT

The aim of this investigation was to evaluate the effect of continuous and intermittent feeding strategies on the efficiency of shallow horizontal subsurface-flow constructed wetlands (SSF CWs). Two experimental SSF CWs planted with common reed were subjected to a three-phase, 10-month experiment involving a common source of settled urban wastewater with a flow rate of 20 L/day during the first and second phases and 30 L/d during the third. In the first and second phases one SSF CW was fed continuously while the other was fed intermittently. In the third phase both systems were operated intermittently, but in one the macrophyte aboveground biomass was cut in order to study the effect of vegetation on removal efficiency. The intermittently fed system presented systematically more oxidized environmental conditions and higher ammonium removal efficiencies (on average 80 and 99% for the first and the second phases respectively) compared with the continuously fed system (71 and 85%). Sulphate removal was higher in the continuously fed system (on average 76 and 79% for the first and second phases respectively) compared with the intermittently fed system (51 and 58%). In the third phase the wetlands that operated with aboveground biomass exhibited more oxidized environmental conditions and better removal efficiencies (on average 81% for COD and 98% for ammonium) than the wetland operated without aboveground biomass (73% for COD and 72% for ammonium). The results of this study indicate that a very high level of ammonium removal could be achieved in a shallow SSF CWs operated with an intermittent feeding strategy.

5.2. INTRODUCTION

The contaminant removal efficiencies attained in horizontal subsurface-flow constructed wetlands (SSF CWs) depend on the oxidation-reduction conditions and gradients prevailing within the systems (Kadlec et al., 2000). This trend has been clearly demonstrated for contaminants such as ammonium, the removal of which requires the establishment of oxygen-enriched zones (García et al., 2005; Wiessner et al., 2005a). The redox state present in SSF CWs is influenced by a variety of factors including organic load, mode of operation (batch, continuous or intermittent), type and development of macrophytes, and water depth (Kadlec and Knight, 1996; García et al., 2004a).

Several studies have been devoted to evaluating the effect of the mode of operation on redox conditions and the removal efficiency of SSF CWs. In general, batch operation promotes more oxidized conditions and therefore better performance than continuous operation. Stein et al. (2003) observed an ammonium removal

efficiency of 57% in batch-operated experimental systems, in comparison with 42% in continuous systems. In fact, Tanner et al. (1999) reported almost complete removal of ammonium in experimental SSF CWs operated in batch mode with small water level fluctuations. On the other hand, Vymazal and Masa (2003) found that changes in the water level in full-scale SSF CWs, with variations of between 8 and 15 cm, had a positive effect on the elimination of several pollutants, including COD and ammonium. In opposition to all these results, Burgoon et al. (1995) observed that batch operation (3-6 days of fill and drain intervals) did not significantly alter the removal of pollutants in comparison with continuous systems. It is possible that in the experiments conducted by Burgoon et al. (1995) the fill and drain intervals were too long to enable differences to be detected. In fact, Behrends et al. (2001), with a similar experimental set-up, found differences when the wetlands were filled and drained at 1-2 hour intervals.

Strong redox gradients at the microscale within the SSF CWs have been linked to the presence of macrophytes. The measurements of Bezbaruah and Zhang (2004) using microelectrodes in experimental SSF CWs showed that the redox potential at the surface of lateral roots of *Scirpus validus* was higher than that observed in the bulk water. The increased redox potential near the surface of the roots was related to the presence of oxygen released by the plants. Despite the evidence of oxygen release by the macrophytes in SFF CWs, what is less clear is the net contribution of this oxygen to contaminant removal. Tanner (2001) reviewed several studies in which planted and unplanted SSF CWs were compared; he concluded that macrophytes only marginally increase the rate of elimination of organic matter but clearly increase the rate of removal of ammonium.

Recent investigations have clearly demonstrated that water depth affects the redox conditions and the removal efficiency of SSF CWs. García et al. (2005) found that pilot SSF CWs with a mean water depth of 0.27 m exhibited higher redox potential values than systems with a water depth of 0.5 m. In addition, the shallower SSF CWs were more efficient for removing COD and ammonium. Headley et al. (2005) observed that doubling the water depth of SSF CWs resulted in no improvement of BOD₅ removal and a decline in total nitrogen removal. In previous studies conducted in our laboratory, in which shallow experimental SSF CWs were fed intermittently (to avoid solid sedimentation and adsorption onto the walls of influent tanks and pipes), it was observed that the removal efficiencies for COD and ammonium were quite high, averaging 80 and 90% respectively (Caselles-Osorio and García, 2006a). While the results were encouraging, particularly for ammonium, it was not clear whether the intermittent feeding strategy had a positive effect on removal efficiency. Thus, in the present study, the performance of two experimental shallow SSF CWs, one of which was fed intermittently and the other continuously, was compared in order to evaluate the influence of the

hydraulic regime (mode of operation) on contaminant removal efficiency. At the end of the experiments the aboveground macrophyte biomass was cut in one of the SFF CWs in order to evaluate the effect of plants on removal efficiency.

5.3. MATERIAL AND METHODS

The two SSF CWs used in this study (named A and B) consisted of plastic containers (1.1 m long, 0.7 m wide and 0.38 m high) filled with gravel extracted from a pilot SSF CW system located in Les Franqueses del Vallès, Barcelona, Spain. A detailed description of the pilot system can be found elsewhere (García et al., 2004a; 2005). Each container had a drainage pipe located on the flat bottom for effluent discharge. The gravel layer (D₆₀=3.5 mm, C_u=1.7 and porosity of 40%) was 0.3 m deep and the water level was kept 0.05 m below the gravel surface to give a water depth of 0.25 m. One vertical, perforated tube was inserted into the gravel near the inlet zone of each wetland system to enable measurements of various physical and chemical parameters. This tube, which was made of metal mesh and that perforated along its entire length, was installed at the bottom of the SSF CWs. The SSF CWs were planted in June 2005 with developed rhizomes of common reed (*Phragmites australis*) and placed on the roof of the building of the Department of Hydraulic, Maritime and Environmental Engineering (Technical University of Catalonia, Barcelona, Spain). By September 2005 the plants were well established and covered the entire surface of the wetlands. The experiments started in October 2005.

The two SSF CWs were fed with settled urban wastewater, which was obtained on a daily basis from the municipal sewer located near the Department building. Experiments were conducted during a period of 10 months and included three phases of operation, in which the hydraulic regime (intermittent or continuous feeding) and the presence of macrophyte aboveground biomass were tested (Table 5.1). Intermittent feeding was carried out on a daily basis by pouring the corresponding amount of settled fresh wastewater into the inlet zone over a period of 20 min. Continuous feeding was achieved by means of a peristaltic pump that conveyed the settled fresh wastewater from a storage tank to the SSF CW. The effect of the hydraulic regime was studied in Phases I and II, in which a flow of 20 L/d was used to give a nominal hydraulic retention time (HRT) of 3.3 days. Note that Phases I and II only differ in the fact that the hydraulic regimes were reversed between the SSF CWs. Thus, both SFF CWs were operated in intermittent and continuous feeding depending on the phase. This strategy was established in order to confirm that the findings were not wetland-specific and really related to the mode of operation.

Table 5.1 Hydraulic regimes, presence/absence of macrophyte aboveground biomass and mean surface loading rates (COD and ammonium) during the three experimental Phases in the two SSF CWs. Note that in the Phase III both SSF CWs were fed intermittently. Inter.: intermittent, Cont.: continuous, Ab.: aboveground.

Wetland	Phase I (Oct – Dec/2005)				Phase II – Apr/200	96)	Phase III (May – Jul/2006)		
	Hydraulic regime	Surface loading rate (g/m².d)		Hydraulic regime	Surface loading rate (g/m².d)		Ab. plant	Surface loading rate (g/m².d)	
	·	COD	NH ₄ +-N		CODD	NH ₄ +-N	- biomass	COD	NH ₄ +-N
SSF CWA	Inter.	7.4	0.67	Cont.	8.5	0.72	Yes	10	1.0
SSF CW B	Cont.	7.4	0.67	Inter.	8.5	0.72	No	10	1.0

The effect of the presence or absence of macrophyte aboveground biomass was studied in Phase III, in which a flow of 30 L/d (intermittently supplied in both SSF CWs) was used to give an HRT of 2.1 days. Note that in this phase it was necessary to increase the flow rate to obtain representative effluent volumes during sampling, as the rate of evapotranspiration was very high at the time of these experiments. Prior to starting this phase, both experimental units were operated intermittently for a period of two weeks to ensure the same initial conditions. When the experiments started both SSF CWs produced effluents with a very similar quality (the ammonium concentration ranged between 1 and 2 mg N/L in the two systems). At this point, the aboveground biomass of SSF CW B was cut to near the level of the gravel, and the short stems remaining were covered with a rubber to reduce the convection of air (diffusion) from the atmosphere to the belowground biomass. This procedure was conducted several times during Phase III to maintain a low aboveground plant biomass in SSF CW B and in turn reduce the amount of oxygen released by the macrophytes.

During the overall study three influent and effluent grab samples were collected at intervals of one week and analyzed immediately for organic matter (COD), ammonium, nitrate, nitrite and sulphates using the methods described in APHA-AWWA-WPCF (2001). In the intermittently fed system, effluent samples were obtained from the water displaced when the influent was added. Water temperature, redox potential (E_H) and dissolved oxygen (DO) measurements were obtained by monitoring the water within the vertical perforated tubes which had been inserted into the gravel at the beginning of the study. Measurements were taken at the midpoint of the water depth and, in the case of the intermittently fed SFF CW, before the feeding process. Water

temperature was recorded with a Checktemp-1 Hanna thermometer, E_H using a platinum-tipped electrode with an Ag/AgCl reference electrode (Cryson 506) and DO with an YSI 50 oxymeter. Evapotranspiration (ET) values were calculated every day from the difference between influent and effluent volumes.

Statistical procedures were carried out using the SYSTAT statistical software package. All of the variables were tested to ensure that they were normally distributed. One-way ANOVA procedures were used to evaluate the effect of the hydraulic regime and the absence/presence of aboveground biomass on COD, ammonium and sulphate mass removal rates. ET was taken into account in the calculation of removal rates that in fact were mass removal loading rates. This was particularly important in Phase III, in which the evapotranspiration rates of the SSF CWs differed between them due to the absence of macrophyte aboveground biomass in SSF CW B.

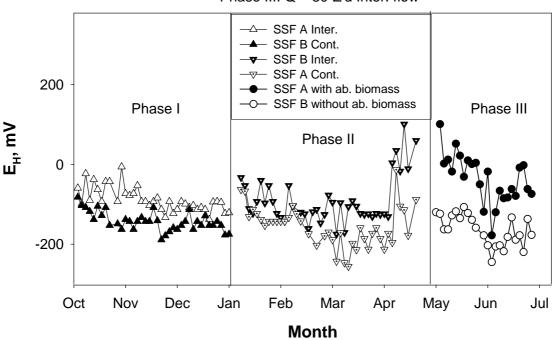
5.4. RESULTS AND DISCUSSION

Effect of intermittent and continuous feeding

The effect of intermittent and continuous feeding was studied in Phases I and II, in which the water temperature in the two experimental units was very similar and averaged arround 14 °C (Table 5.2). The DO concentrations measured at the perforated tubed of the two SSF CWs were usually below the detection limits of the oxymeter. The E_H values were clearly higher in the intermittently fed system than in the continuously fed systems during both phase (Table 5.2 and Figure 5.1). In Phase I the E_H values of the intermittent system ranged from -136 to -6 mV, whereas in the continuous system from -179 to -83 mV. During Phase II, the E_H values ranged from -251 to +101 for the intermittent and -256 to -13 for the continuously fed system. Therefore, the results for E_H indicate that the intermittently fed SSF CW operated in more oxidized conditions than the continuously fed SSF CW. Moreover, this trend was not wetland-specific, since it was detected for both SSF CWs.

Table 5.2 Average values and standard deviations (in brackets) of water temperature, E_H and evapotranspiration for both SSF CWs in Phase I (n = 30) and II (n = 45). Note that in the two Phases each wetland was operated with a different hydraulic regime. Inter.: intermittent, Cont.: continuous.

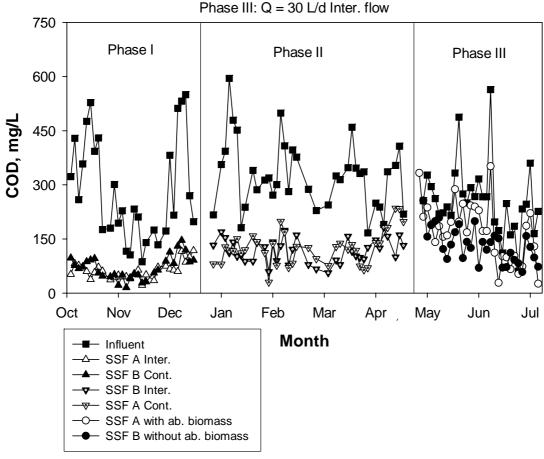
Phase	Tempe (°	erature C)		- н 1V)	Evapotranspiration (mm/d)		
	Inter.	Cont.	Inter.	Cont.	Inter.	Cont.	
1	14 (4)	13 (5)	-89 (30)	-143 (24)	8.4 (4.3)	8.4 (4.3)	
II	16 (̂4)́	14 (̀4)́	-90 (̇̀57)́	-157 (̀48)́	7.7 (4.3)	7.7 (4.3)	



Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow Phase III: Q = 30 L/d Inter. flow

Figure 5.1 Temporal changes in EH in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.) and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

Figure 5.2 show the changes over time of the COD concentrations. The concentration of the COD in the influent was in average $287(\pm 143)$ mg/L for phase I and $326(\pm 94)$ mg/L for II. The COD effluent concentrations during phase I averaged $63(\pm 22)$ and $71(\pm 32)$ mg/L respectively for the intermittently and continuously fed systems. During Phase II, the effluent concentrations for intermittently and continuously fed SSF CWs averaged $119(\pm 33)$ and $125(\pm 46)$ mg/L respectively, being therefore higher than in Phase I. Despite these higher effluent concentrations the mass removal rates were significant in Phase II (Table 5.3). The effluent COD mass loadings were very similar during the two phases in both systems (Table 5.3 and Figure 5.2). In fact, the average COD mass removal efficiencies were not statistically different between both systems according to the ANOVA method (ρ = 0.663). These results indicate that although the intermittently fed SSF CW operated in more oxidized conditions, there was no subsequent clear improvement in COD removal. The amount of organic matter removed in the two phases and the two SSF CWs was on average approximately 6 g COD/m².d. This value is within the range of 5.5 to 10 g/m².d reported by Sikora et al. (1995) in similar systems.



Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow

Figure 5.2 Temporal changes in influent and effluent COD concentrations in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

Table 5.3 Average values and standard deviations (in brackets) of influent (Inf) and effluent (Eff) surface mass loadings (g/m^2 .d) and removal efficiencies (Rem) of COD, ammonium and sulfates in the experimental SSF fed intermittently (Inter.) and continuously (Cont.) during Phases (Ph.) I and II. n = 30 in Phase I and n = 45 in Phase II.

	COD						NH ₄ +-N					SO ₄ =			
Ph.	Inf	E	Eff		em %)	Inf	Ef	f		em %)	Inf	E	ff		em %)
		Inter.	Cont.	Inter.	Cont.	•	Inter.	Cont.	Inter.	Cont.		Inter.	Cont.	Inter.	Cont.
Ī	7.4	1.1	1.2	85	84	0.6	0.005	0.09	99	85	4.8	2.0	1.0	58	79
	(3.7)	(0.6)	(0.7)			(0.3)	(0.004)	(80.0)			(0.7)	(1.5)	(0.7)		
II	8.5	2.4	2.5	71	70	0.7	0.14	0.2	80	71	5.2	2.5	1.2	51	76
	(2.4)	(8.0)	(0.9)			(0.2)	(0.9)	(0.1)			(1.8)	(1.8)	(0.9)		

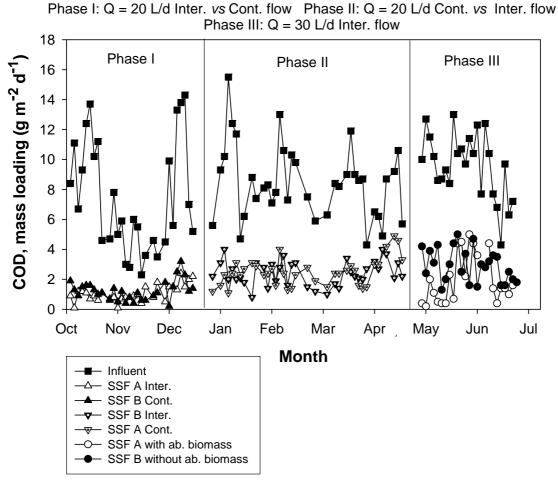
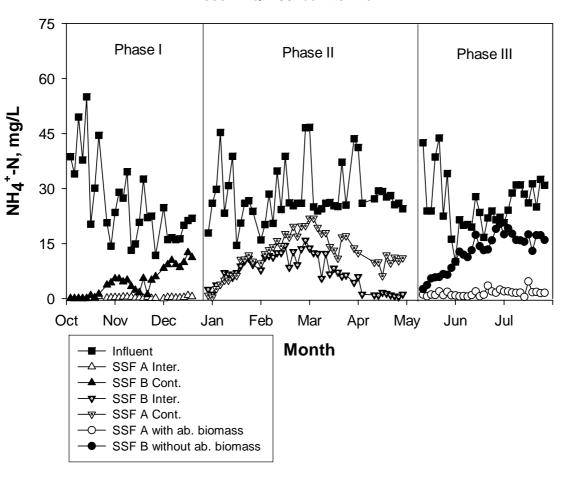


Figure 5.3 Temporal changes in influent and effluent COD mass loadings in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

Figure 5.4 show the changes over time of the ammonium concentrations. The average concentration of ammonium in the influent was $26(\pm 11)$ mg N/L for Phase I and $28(\pm 8)$ mg N/L for II. Average effluent concentrations in Phase I were $0.3(\pm 0.2)$ and $5(\pm 3.9)$ mg N/L in the intermittent and continuously fed systems respectively. During Phase II, the respective effluent concentrations were greater, averaging $7.3(\pm 4.5)$ mg N/L for the intermittent treatment and $12(\pm 5.4)$ mg N/L for the continuously fed system. Nitrates and nitrites were not detected or had a very low concentrations in any of the experimental phases.

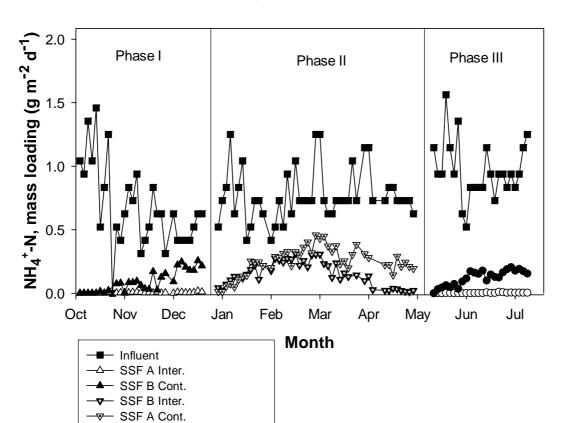


Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow Phase III: Q = 30 L/d Inter. flow

Figure 5.4 Temporal changes in influent and effluent ammonium concentrations in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

The effluent ammonium mass loadings were lower in the SSF fed intermittently than in the SSF fed continuously (Table 5.3, Figure 5.5). The average removal efficiencies were therefore greater in the intermittent system and statistically different (p < 0.001). In both Phases the intermittently-fed SSF averaged an amount of ammonium removed of 0.6 gNH₄+-N/m².d while the continuously-fed SSF averaged 0.4 gNH₄+-N/m².d. From these results is clear that, in opposition to what it was observed for COD, the intermittent feeding strategy improved the removal of ammonium. Note that ammonium mass removal efficiencies were quite high in both SSF; even when they were operated with continuous feeding the removals were higher

than 70%. This high values reported in the present study are commensurated with an earlier report by Caselles-Osorio and García (2006b), in which ammonium mass removal rates in similar shallow SSF systems ranged from 80 to 90 percent. These high removal efficiencies are notable, given that ammonium removal efficiencies in horizontal SSF are usually lower than 50% (USEPA, 2000).



SSF A with ab. biomassSSF B without ab. biomass

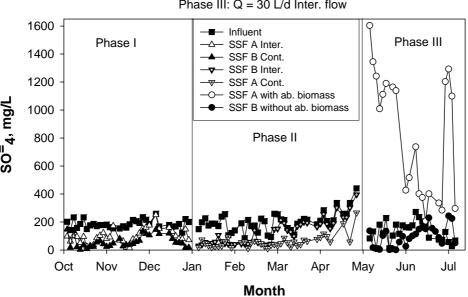
Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow Phase III: Q = 30 L/d Inter. flow

Figure 5.5 Temporal changes in influent and effluent ammonium mass loadings in the two SSFsystems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.)), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

The temporal changes of the effluent ammonium mass loadings showed certain patterns that were not seen for COD (Figure 5.3). At the beginning of Phase I both SSF had approximately the same effluent ammonium loadings; nevertheless, the loadings of the continuously-fed system increased progressively until the end of this Phase. When the feeding strategies were reversed in Phase II, the SSF B (that passed from continuous to intermittent) suddenly produced effluents with low ammonium mass loading. On the other hand, the effluent loadings progressively increased in SSF A in Phase II (continuous) as it was observed for SSF B in Phase I. On the contrary to what it was observed in Phase I, the effluent ammonium loadings of the intermittent system (SSF B) increased progressively until March (with the same pattern as observed for the continuously-fed system). This increase occurred at the same time that the all aboveground biomass of the macrophytes was dry because of the winter (January to March). From March the effluent loadings of the intermittent system decreased to reach almost zero values while in the continuous system the loadings maintained in higher values.

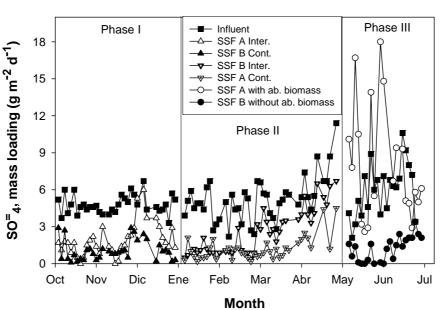
During both Phases, the effluent concentrations of sulfate were always greater in the intermittently fed system as compared to the continuously fed system (Figure 5.6). The average concentration of sulphate in the influent was $183(\pm 28)$ mg/L for Phase I and $200(\pm 68)$ mg/L for II. During both phases, the effluent concentrations of sulphate were always greater in the intermittently fed system than in the continuously fed system. Thus, in Phases I and II the effluent concentrations for the intermittently fed SSF CW were $103(\pm 56)$ and $127(\pm 90)$ mg/L respectively, while the corresponding values for the continuously fed SSF CW were $60(\pm 38)$ and $59(\pm 47)$ mg/L respectively.

The effluent sulfate mass loading was significantly higher in the intermittently fed systems than in the continuous systems (Table 5.3, Figure 5.7). The average mass removal rates were lower in the intermittently fed system and statistically different (ρ < 0.001). In both Phases the intermittently-fed SSF averaged an amount of sulfate removed of 2.8 g/m².d while the continuously-fed SSF averaged 3.9 g/m².d. The lower removal rates observed in the intermittently-fed system are related with the more oxidized conditions detected in this SSF. Note that the effluent sulfate mass loadings were very similar in both SSF in Phase II from January to March, when the effluent ammonium mass loadings were also very similar (Figure 5.4).



Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow Phase III: Q = 30 L/d Inter. flow

Figure 5.6 Temporal changes in influent and effluent sulfate concentrations in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.)), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.



Phase I: Q = 20 L/d Inter. vs Cont. flow Phase II: Q = 20 L/d Cont. vs Inter. flow Phase III: Q = 30 L/d Inter. flow

Figure 5.7 Temporal changes in influent and effluent sulfate mass loadings in the two SSF systems according to the feeding strategy (continuous (Cont.) or intermittent (Inter.)), and presence or absence of aboveground plant biomass (ab. biomass). Note that the feeding strategies were reversed in Phases I and II and both SSF were fed intermittently in Phase III.

From the results of this study it is clear that the intermittent feeding strategy gives place to a more oxidized environment that in turn improves the removal of ammonium. The more oxidized conditions may be due to three non exclusive reasons: the hydrodynamic behavior, water level fluctuations and macrophyte-mediated effects. The mode of feeding affects the hydrodynamic behavior of the system and subsequently the redox conditions. In the intermittently fed wetland the daily wastewater flow (20 L/d) was poured in 20 min causing more internal turbulence and mixing than in the continuous system. The occurrence of laminar or turbulent flow in SSF can be determined using the Reynolds number: Rn = Vd/u, where the V is the flow per unit of transverse area (in m/s), d is the average diameter of the substrate (in m) and u is the water kinematic viscosity (in m²/s). The flow is laminar when Rn <1; turbulent when Rn >10; and transitional when Rn is between 1 and 10. The Reynolds numbers were 0.017 for the continuously-fed system, and 1.2 for the intermittently-fed system (in this case when the influent was added). Thus, the greater turbulence in the intermittently-fed SSF would tend (in the moment of wastewater addition) to transport more surface diffused oxygen and oxygen released by the roots (located near the roots in aerobic microsites) to anaerobic zones and therefore providing a more oxidized bulk water environment. Also it is possible (and not incompatible with the hypothesis described above) that the higher turbulence give opportunity to a greater amount of water to pass through aerobic and anaerobic microsites while more laminar conditions in the continuous system gives place to some water volumes to pass only though anaerobic sites, specially at the bottom of the wetland.

The intermittent method of feeding resulted in slight greater fluctuations of water depth (in relation with the ET) than the continuous system that in turn may had been related with the more oxidised conditions. When the water is added in the intermittent system the water level is 0.25 m and from then starts to decrease according to the ET rate. In the continuous system the relative decrease is lower because the wetland receives inflow during all day. Estimations of water level changes (in fact decreases) in Phases I and II considering the lowest and the highest ET rates gave a result of 9.5 and 19 mm for the intermittent system and 1.3 and 6.9 mm for the continuous. Breen (1997) reported on batch vs. continuous wetland systems that the ET caused level fluctuations on the batch-loaded system. These fluctuations exposed a higher amount of the granular medium to atmospheric favoring more oxidised conditions. Behrends et al. (1993) reported reaeration rates four times faster in drain and fill treatments than in static controls, due to the rapid oxygenation of the wetted gravel that was exposed to atmospheric oxygen during the drain phase.

A macrophyte effect may also be behind the more oxidized conditions of the intermittently fed system. Bezbaruah and Zhang (2004) observed that the DO at the root surface of Scirpus validus increased with the

oxygen demand of the surrounding bulk water. Thus, it is possible that, because when the wastewater is added to the intermittent system a greater volume of the reactor is in contact with wastewater than in the continuous system. As a result this greater volume is exposed to a comparatively higher load and therefore a higher amount of oxygen is released by the macrophytes, which contributes to the more oxidized conditions.

Effect of the macrophytes

This was studied in Phase III when the aboveground macrophyte biomass of SSF B was cut. During this Phase the average water temperature inside the SSF was warmer than in the previous Phases and the very high ET recorded in this Phase was related with the high temperatures (Table 5.4). Note that ET was lower in SSF B because the lack of aboveground biomass. The E_H values were clearly higher in the SFF with aboveground biomass than in the other system (Table 5.4 and Figure 5.1). The E_H values ranged from -178 to +101 mV in the SSF with aboveground biomass, and from -245 to -35 mV for the other system. Therefore the results of the E_H indicate that the SSF with aboveground biomass operated in more oxidized conditions than the other SSF. This trend has been already reported in other studies such that of Burgoon et al. (1995) in which planted and unplanted systems has been tested.

Table 5.4 Average values and standard deviations (in brackets) of water temperature (Temp.), E_H, ET, influent (Inf) and effluent (Eff) surface mass loadings (g/m^2 -d) and removal efficiencies (Rem) of COD, ammonium and sulfates in the experimental SSF during Phase III. n = 29.

	Temp E _H		E _H ET -	COD				NH ₄ +-N		SO ₄ =		
SSF	(°C)	(mV)	(mm/d)	Infl	Effl	Rem (%)	Infl	Effl	Rem (%)	Infl	Effl	Rem (%)
Plants	26 (1.4)	-35 (61)	23.4 (9.5)	10 (3.8)	1.9 (1.5)	81	1 (0.3)	0.019 (0.016)	98	5 (2.7)	8.8 (5.3)	-
No plants	26 (1.4)	-164 (38)	16.8 (6.2)	10 (3.8)	2.7 (1.1)	73	(0.3)	0.28 (0.12)	72	5 (2.7)	1.4 (1.1)	72

The effluent concentrations of COD in the system with plant biomass averaged 172 mg/L as compared to 132 mg/L for the system without plant biomass. Likewise, the effluent ammonium concentrations averaged 1.5 mg/L for the system with plant biomass and 13 mg/L for the system without plant biomass. The effluent COD and ammonium mass loadings were lower in the SSF with aboveground biomass than in the other (Table 5.4, Figures 5.3 and 5.5). The average COD and ammonium mass removal efficiencies were statistically different between both SSF (p < 0.001). The amount of organic matter removed was in average about 8.1 g COD/m².d

for the system with aboveground biomass and 7.3 g COD/m².d for the system without aboveground biomass. The amount of ammonium removed was in average 0.96 gNH₄+-N/m².d in the SSF with aboveground biomass and 0.68 gNH₄+-N/m².d for the other SSF. Note that effluent ammonium mass loading increased progressively in the SSF without aboveground biomass (Figure 5.5), and in a similar way to what it was observed in Phase I for the SSF fed continuously. From these results it is clear that the more oxidized conditions in the SSF with aboveground biomass improved the removal of COD and ammonium.

The changes over time effluent concentrations of sulfates in the system with plant biomass averaged 933 mg/L as compared to 97 mg/L for the system without plant biomass. The effluent sulfate mass loading was clearly higher in the system with aboveground biomass than in the other system (Table 5.4 and Figure 5.7). If fact, this loading was extraordinary high in the SSF with aboveground biomass, with many values greater than the influent sulfate loading (Figure 5.7). This extraordinary loading is linked with a high redox potential in conjunction with a high evapotranspiration (in comparison to the SSF without aboveground biomass). Under the prevailing redox conditions in the SSF with aboveground biomass sulfate was not removed by sulfate reduction and concentrated due to high evapotranspiration rate. Furthermore, some of the solid phase sulphides that had been deposited as a result of sulfate reduction during Phases I and II, were subsequently oxidized in the Phase III due to the significantly higher redox values in the treatment with aboveground biomass. Reduced sulphur formed during sulfate reduction can be stored in sediments either as metal sulphides, or as organic sulphur compounds. These compounds can be oxidized by chemosynthetic bacteria using oxygen as electron acceptors and fixing carbon dioxide (Howarth et al., 1992). This tendency for sulfate to be conserved and concentrated in wetland environments has been observed by other authors previously and is clearly correlated with a decrease in the activity of sulfate reducing bacteria (King, 1988; Choi, 2006).

In the present study when the aboveground biomass was cut in one of the SSF the convective transport of oxygen from the aerial parts to the roots and rhizomes was reduced, the water redox potential decreased and subsequently the removal of COD and ammonium diminished. Moreover, the sulfate had a higher removal rate than in the system with aboveground biomass according with the more reducing conditions in the system without aboveground biomass. Thus, in the conditions tested in this study it is clear that the macrophytes have a clear impact on the removal efficiency of COD and ammonium. This result is in agreement for ammonium with the findings of the researches reviewed by Tanner (2001) on planted and unplanted systems. Note that ammonium is a contaminant which removal is highly dependant on the redox conditions. In the case of COD most of the previous studies indicate that macrophytes provide only negligible improvements (Tanner, 2001). It is possible that the effect of the macrophytes on the treatment is affected by

the experimental conditions used in each particular investigation, and for example the shallow depth of the wetlands used in the present study promotes the macrophyte contribution on the COD removal.

The COD removal was affected by the presence or absence of macrophyte aboveground biomass while it was not by the continuous or intermittent mode of operation, although both treatments caused changes in the redox potential. We do not know the reasons behind these two patterns; nevertheless, it is worthy to note that the differences in redox potential between the SSF when the effect of the macrophyte was studied (in average 92 mV) were greater than when it was studied the feeding strategy (in average 51 and 56 in Phase 1 and 2 respectively).

In the present study we observed that the higher redox values in the intermittently-fed systems were correlated with enhanced removal of ammonium, but reduced levels of sulfate removal in comparison to the continuously-fed systems. This inverse relationship between ammonium removal and sulfate removal has been described in other studies (García et al. 2004a, 2005; Wiessner et al., 2005b). Wiessner et al. (2005b) reported that this inverse relationship coincides with high concentrations of organic matter and sulfate in the influent wastewater, and indicated that reduced sulfur compounds, such as hydrogen sulfide, are known to be potent inhibitors of plant growth and certain microbial activities, including nitrification. In fact these authors observed an exponential decrease in ammonium removal from 75% to 35% in conjunction with an increase of sulfate removal (50% removal).

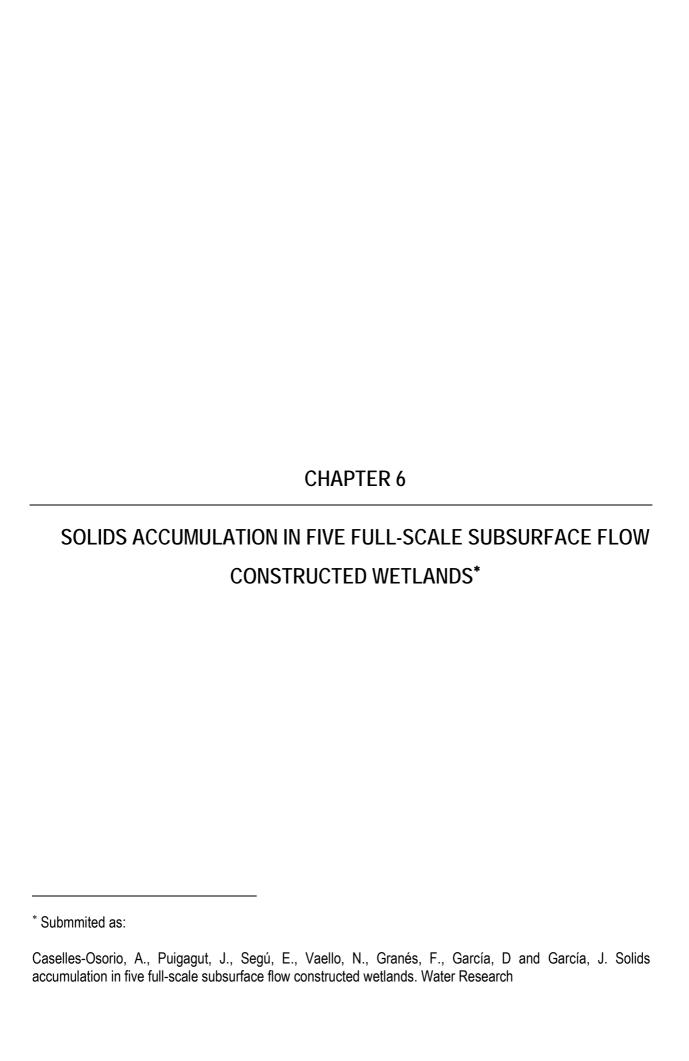
The results obtained in the present study are in agreement with those of Stein and Kakizawa (2005) and others reported in the Introduction section in which it has been observed that batch loading improves the contaminant removal efficiency in comparison to continuously fed systems. However, it should be taken into account that batch and intermittent operation are not the same because the batch mode involves complete draining the wetland, while this is not the case in the intermittent mode used in this study. Certainly, batch systems receive the influent intermittently, but the tested SSF were not periodically drained (changes in water level only occurred as a result of the ET). The intermittent feeding mode as performed in this study constitutes a very unusual way for feeding a SSF. In view of our results, and specially if ammonium should be removed, intermittent feeding should be considered for full scale projects. Future experiments should deal on the effect of discharging the wastewater in several discharges instead of one as it was done in this study.

5.5. CONCLUSIONS

The main conclusion of this investigation is that intermittent feeding in shallow SSF provided a more oxidized treatment environment in comparison to continuous feeding that in turn promoted a greater removal of ammonium (in average 80-99% in front of 71-85%) and a lower removal of sulfate (in average 51-58% in front of 76-79%).

In addition, it was observed that the presence of macrophyte aboveground biomass caused a more oxidized environment in comparison to SSF without such biomass that subsequently in turn enhanced the removal of COD (in average 81% in front of 73%) and ammonium (in average 98% in front of 72%). The removal of sulfate was greater in the system without the macrophyte aboveground biomass.

This investigation, together with previous studies conducted by the authors, has corroborated that significant ammonium removal (> 80%) can be achieved in shallow horizontal SSF systems, and that the level of ammonium removal can be enhanced through intermittent feeding.



6.1. ABSTRACT

In this study, we evaluated the amount of accumulated solids in six different horizontal subsurface flow constructed wetlands (SSF CWs). We also investigated the relationship between accumulated solids and, on one hand, the wastewater quality and load and, on the other hand, the hydraulic conductivity of the granular medium. Aerobic and anaerobic biodegradability tests were also conducted on the accumulated organic matter. Experiments were carried out on full scale wastewater treatment systems consisting of SFF CWs in series with stabilisation ponds, which are used for the sanitation of small towns in north-eastern Spain. There were more accumulated solids near the inlet of the SSF CWs (3-57 kg/m²) than near the outlet (2-12 kg/m²). Annual solids accumulation rates ranged from 0.9 to 3.6 kg/m².year, and a positive relationship was observed between accumulation rates and loading rates. Most of the accumulated solids had a low level of organic matter (<20%). The results of the aerobic and anaerobic tests indicated that the accumulated organic matter was very recalcitrant and difficult to biodegrade. The hydraulic conductivity values were significantly lower near the inlet zone (0-4 m/d) than in the outlet zone (12-200 m/d). Although hydraulic conductivity tended to decrease with increasing solids accumulation, the relationship was not direct. One major conclusion of this study is that the improvement of primary treatment is necessary to avoid rapid clogging of the granular media due to solids accumulation.

6.2. INTRODUCTION

The use of subsurface flow constructed wetlands (SSF CWs) for treating municipal wastewater in small communities of less than 2000 persons-equivalent (pe) is growing rapidly in many regions of the world. Southern Europe is not an exception, and examples of this trend are the more than 300 facilities have been put in operation in Portugal (Dias and Martins-Dias, 2003) and 400 in France (Molle et al., 2005) in recent decades. In the future, these numbers are expected to increase in all Mediterranean countries because SSF CWs have several advantages over conventional mechanical sanitation systems for small communities where land availability and cost are not limiting factors (García et al., 2001), including low energy requirements, operation and maintenance that may be conducted by unskilled staff, and low sludge production.

In Catalonia, north-eastern Spain, the Water Agency has constructed a dozen SSF CW systems since the year 2000. These systems are usually a combination of horizontal flow wetlands and maturation ponds.

During the initial years of operation, these facilities have generally shown adequate removal efficiencies for total suspended solids (TSS, <35 mg/L) and BOD (<25 mg/L) (Robusté, 2004). However, most horizontal SSF CWs show a certain degree of ponding near the inlet, which indicates rapid clogging of the granular medium. Clogging is the worst operational problem of SSF CWs, as has been reported in regional operation and maintenance analyses (Rousseau et al., 2004a). It is a complex process, due to the accumulation of different types of solids (Blazejewski and Murat-Blazejewska, 1997). Solids accumulate within the surface layers and on top of the granular medium as sludge, and represent a mixture of wastewater solids, and plant and microbial detritus (Tanner et al., 1998).

Although solids accumulation is a major aspect of wetland technology application, few detailed studies have been devoted to the quantification and characterisation of accumulated solids. In five-year old pilot horizontal SSF CWs (treating dairy wastewater with a load ranging from 2.2 to 7.3 g TSS/m².day), Tanner et al. (1998) measured much higher accumulation rates for organic solids (1.3 to 3.0 kg volatile suspended solids (VSS)/m².year) than for organic solids potentially contributed by applied wastewaters (0.4 to 1.6 VSS/m².year). Thus, sources of solids other than wastewater, in particular those of plant origin, were also important for the total solids mass balance in this study. In fact, in a previous study of the same pilot system, Tanner and Sukias (1995) showed the importance of this plant-derived solids contribution, with a 1.2 to 2.0 kg VSS/m² increase in organic solids accumulation in planted SSF CWs over equivalent unplanted beds over a period of two years. Nguyen (2001) studied the same pilot system evaluated by Tanner and Sukias (1995) and Tanner et al. (1998) and found that up to 90% of the organic solids were composed of recalcitrant fractions, probably originating from lignocellulose, as reported by the author.

The accumulation rates of organic solids seem to decrease with the maturation time of SSF CWs. For example, Tanner et al. (1998) observed that for the first two years of operation the rates were approximately twice as high as in the next three years. On the other hand, with respect to seasonal variations, Chazarenc and Merlin (2005) did not observe a clear trend for seasonal variations in the accumulated solids in vertical SSF CWs. In theory, the progressive increase in solids accumulation in SSF CWs over time is associated with the trend of decreasing the hydraulic retention time. However, the available data indicate that this relationship is not direct and it seems that other factors, such as the bulk density characteristics of the solids (related to the proportions of labile, stable and inert solids fractions) and the spatial patterns of the accumulations, mediate the effects on hydrodynamic behaviour (Tanner et al., 1998; Nguyen, 2001).

This study aimed to determine the amount of accumulated solids in the granular medium of six full-scale SSF CWs (in five different treatment plants). We also investigated the relationship between accumulated solids

and, on one hand, the wastewater quality and load and, on the other hand, the hydraulic conductivity of the granular medium. In two SSF CWs, we also tested the aerobic and anaerobic biodegradability of the accumulated organic matter. The results of this investigation should contribute to obtain practical recommendations for preventing or reducing the clogging process.

6.3. MATERIAL AND METHODS

The sampling campaigns, measurements and experiments were conducted from November 2005 to March 2006.

SSF CW systems

The five SSF CW systems treat the municipal wastewater of four small towns in the province of Lleida (Catalonia, north-eastern Spain): Alfés, Almatret (at this place two CW systems, northern and southern), Corbins and Verdú. All of these systems are operated and maintained by Aigües de Catalunya, S.A. The climate at these sites is continental Mediterranean, with an average annual temperature of 14.4°C and accumulated rainfall of 606 mm (data for 2003, Catalan Meteorological Service, Lleida-Raimat station, www.meteocat.com). The systems in Alfés, Corbins and Verdú started to operate in 2002, whereas the two plants in Almatret in 2003. Table 6.1 shows some important characteristics of the SSF CWs used in this study.

Table 6.1 General design characteristics of the SSF CWs evaluated in this study. Note that in Verdú two wetlands were evaluated.

System	Served	Mean	Surface	Aspect	Subst proper		Porosity	Mean Water
	population equivalent	flow rate (m³/d)	area (m²)	ratio	D ₆₀ (mm)	Cu	(%)	depth (m)
Verdú 1	2000	177	976.5	1:1.1	9.0	1.8	40	0.5
Verdú 2	2000	177	518	1:2	9.0	1.8	40	0.4
Alfés	290	60	1235	1.15:1	10.0	2.5	34	0.5
Corbins	2000	218	1225	1:1	9.2	1.8	38	0.5
Almatret north	164	25	467	1:1.25	8.98	1.8	39	0.5
Almatret south	373	57	500	1:1	8.9	1.8	39	0.5

 $^{^1}$ D₆₀ is the the diameter at which 60% of the material passed through the sieve. C_u is the uniformity coefficient C_u = D₆₀/D₁₀.

1. Verdú (Figure 6.1): This system has one septic tank, from which the primary effluent is distributed to four parallel horizontal SSF CWs planted with common reed (*Phragmites australis*). After the SSF CWs, there are two maturation ponds with a depth of 1.0 m, followed by two smaller polishing horizontal SSF CWs. Samples for the organic matter quantification and hydraulic conductivity measurements were obtained from two SSF CWs called Verdú 1 (located after the septic tank) and Verdú 2 (located after one of the ponds).

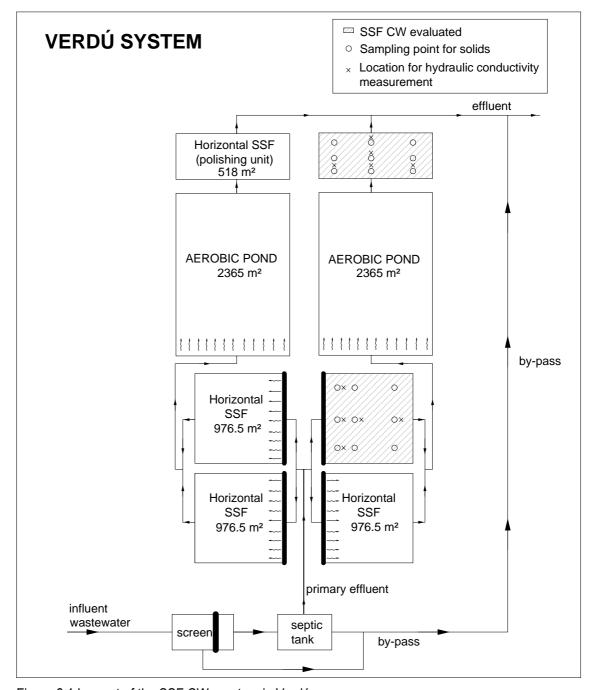


Figure 6.1 Lay-out of the SSF CWs system in Verdú.

Alfés (Figure 6.2): This system has one septic tank, from which the primary effluent is distributed to
two horizontal SSF CWs in series planted with common reed. There is an aerobic pond with a
water depth of 1.6 m for effluent polishing. The first SSF CW was used for organic matter and
hydraulic conductivity measurements.

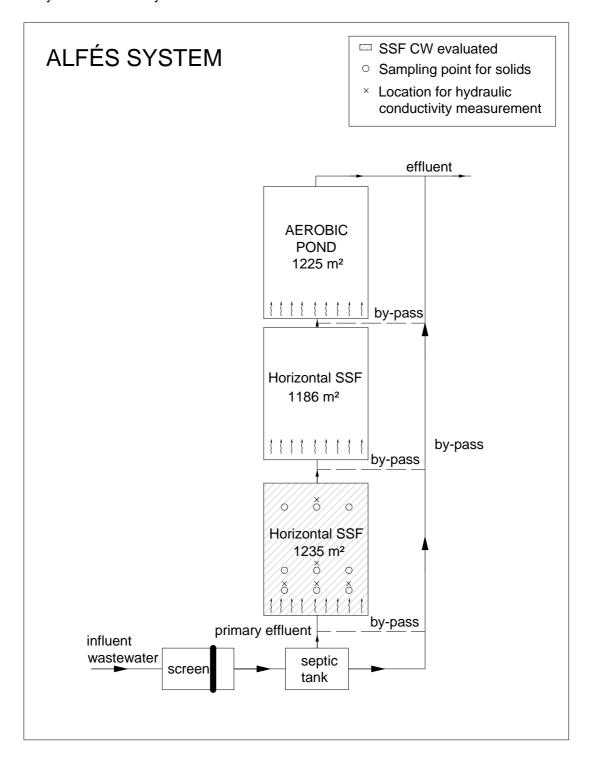


Figure 6.2 Lay-out of the SSF CWs system in Alfés.

3. Corbins (Figure 6.3): In this system, the wastewater is not pretreated and flows directly to an Imhoff tank, from which the primary effluent is equally distributed to two parallel horizontal SSF CWs planted with common reed. After the SSF CWs, there are three ponds in series (one facultative pond with a water depth of 1.5 m and two aerobic ponds with a water depth of 1.0 m). The effluent of the last pond is conveyed to another horizontal SSF CW followed in series by three intermittent sand filters. One of the two parallel SSF CWs was used for this study.

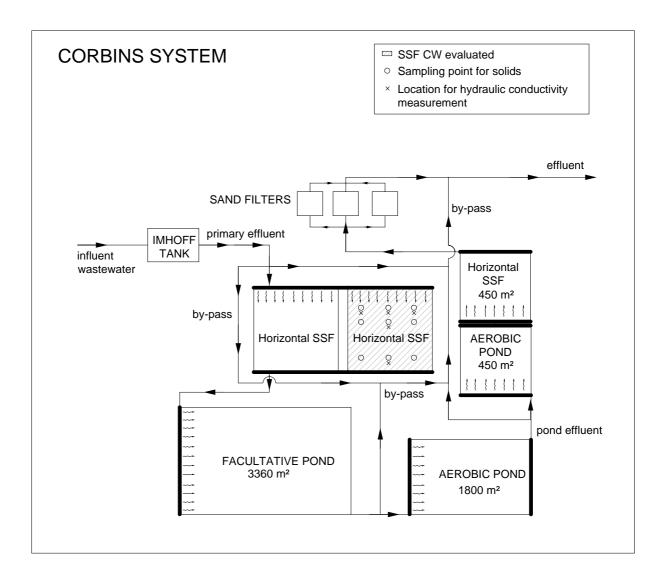


Figure 6.3 Lay-out of the SSF CWs system in Corbins.

4. Almatret north (Figure 6.4): This system treats approximately a 30% of the town's wastewater flow. It has a septic tank followed by one SSF CW planted with common reed and an aerobic pond (0.5 m deep) in series.

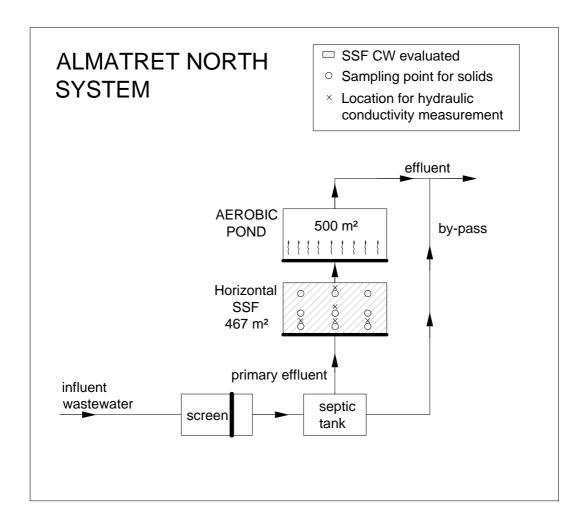


Figure 6.4 Lay-out of the SSF CW system in Almatret north.

5. Almatret south (Figure 6.5): This system treats the remaining 70% of the flow by means of a septic tank and two parallel SSF CWs planted with common reed. After the CWs, the wastewater flows to three aerobic ponds with a water depth of 0.5 m. In this system, one of the long sides of the two SSF CWs is slightly bent.

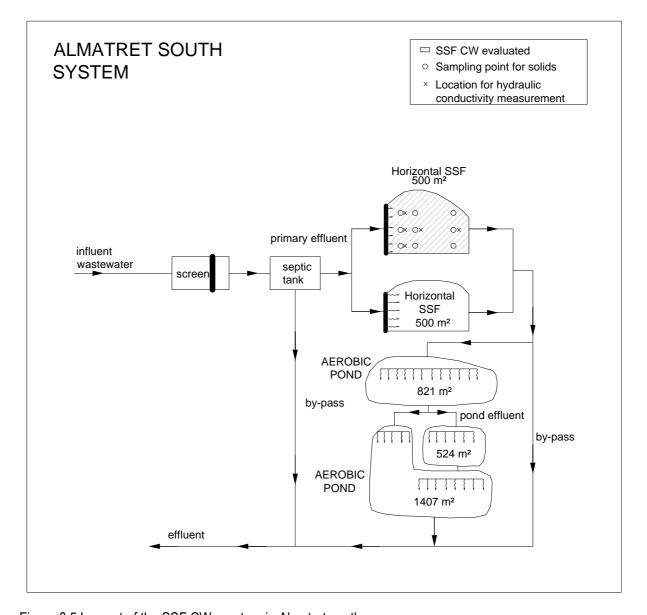


Figure 6.5 Lay-out of the SSF CWs system in Almatret south.

The different configurations of these treatment plants are not the result of particular technical criteria. Rather, they seem to be related to the preferences of the designers.

Wastewater samples and analyses

Three sampling campaigns were conducted at each plant during the period of study in order to examine the pollutant-removal role of the wetlands (and the other unit processes) within the wastewater treatment plants. Influent and effluent grab samples of each unit process were analysed in terms of COD (total and filtered at 1.2 μ m and 0.2 μ m) and ammonium according to APHA-AWWA-WPCF (2001). The fractions of the COD were calculated as follows: COD_{settleable and macrocolloidal} = COD_{total} - COD_{1.2 μ m}, COD_{colloidal} = COD_{1.2 μ m}, COD_{dissolved} = COD_{0.2 μ m}. Some colloids are smaller than 0.2 μ m, but for practical purposes we will consider "colloids" the particles between 1.2 μ m and 0.2 μ m (as already described by Marani et al., 2004). Aigües de Catalunya S.A. provided historical records on plant performance in terms of total COD and BOD₅.

Accumulated solids samples and analyses

The samples were taken once during the overall period from the six SSF CWs evaluated (Figures 6.1-6.5). At each wetland, three stretches were considered. The first two were placed 2 and 4 m from the inlet respectively, and the third one was placed 2 m from the outlet. The two inlet zone stretches were placed very close to each other because we expected that the accumulated solids would decrease drastically between the first and the second. Within each stretch, three evenly distributed sampling points were considered. To obtain the samples, a sharpened steel tube (200 mm in diameter and 400 mm long) was almost completely inserted into the gravel at each point using a mallet. After that, the gravel inside the tube was carefully removed up to a wetted depth of 20 cm using a gardening shovel. Gravel samples were obtained from the gravel at a wetted depth of 20-30 cm, which is approximately the mean depth in all wetlands. The samples were stored in plastic bags, transported to the laboratory in a refrigerated container and processed within the next 24 hours.

In this study, we considered two types of accumulated solids: interstitial solids (which includes those entrapped in the empty spaces between the gravel and which are easily released when the gravel loses its spatial structure) and adhered solids (which are clearly linked to the gravel particles and are not easily released). The interstitial solids were measured in terms of TSS and VSS after manually shaking the gravel together with interstitial water. The adhered solids were analysed after releasing the interstitial solids from 120 g of gravel samples, to which 100 mL of tap water was added. These samples were subjected to ultrasounds (*P*-Selecta) for 7 minutes (Morató et al., 2005). All solids analyses were conducted according to

APHA-AWWA-WPCF (2001). The adhered solids content was estimated with the same methods used for interstitial solids. The accumulated solids were calculated as the sum of the interstitial and adhered solids.

Hydraulic conductivity measurements

These measurements were taken once at each plant and in the wetlands from which the accumulated solids were quantified. The measurements were obtained from five points placed very close to the points from which the organic samples were obtained: three evenly distributed points within the first stretch of the wetlands and two points in the middle of the second and third stretches (Figures 6.1-6.5). Hydraulic conductivity was estimated using the falling-head test method (NAVFAC, 1986). We used the procedure described in Caselles-Osorio and García (2006a), but with a bigger tube (700 mm long and 200 mm in internal diameter). Briefly, the tube is inserted 250 mm into the gravel, filled with water in a pulse, and the decrease in the water level is detected by a pressure probe connected to a computer by means of a data taker.

Accumulated organic matter biodegradability tests

The aerobic and anaerobic biodegradability of the accumulated organic matter was evaluated from the SSF CWs in Verdú (wetland 1) and Alfés. Gravel samples (including interstitial water) for the tests were collected in the inlet zone, where, in previous sampling campaigns, more accumulated solids were observed than in the outlet zone. The samples were obtained by using a shovel to manually extract the gravel from approximately 20 cm below the water surface and storing the samples in a plastic bag for further analysis.

Aerobic biodegradation activity was evaluated by measuring COD variations over time and without oxygen limitation. Anaerobic activity was evaluated by measuring the methane accumulation in the headspace of the bottles used for the experiments. Aerobic tests were conducted using two cylindrical methacrylate reactors (one for each sample) with a diameter of 200 mm and a height of 400 mm. Both reactors were equipped with a membrane fine bubble diffusser located on the bottom that was connected to an air fish-tank pump that provided aeration and mixing. Each reactor was filled with 6 L of interstitial water, which was continuously aerated and kept at room temperature. The experiments were conducted without gravel in order to ensure the complete aeration of the tanks and because 99% of the organic matter remained in the interstitial fraction of the samples (whereas 1% adhered to the gravel media). During the experiments, the oxygen concentration in the bulk liquid was always greater than 8 mg/L. The samples for the COD and VSS analyses were taken

from the reactor twice a day for 25 days. This period was considered long enough to ensure the complete removal of the readily and slowly biodegradable organic matter.

The anaerobic tests were conducted using four dark, airtight 2.9 L glass bottles (two per sample) with a screw top and a microvalve for gas extraction. The bottles were filled with 4 kg of gravel and 600 mL of interstitial wastewater, offering a headspace of 650 mL for gas accumulation. The air remaining in the headspace was removed by injecting He for 15 minutes. The four bottles were placed in dark chambers. Two of them were kept at 5°C and two at 20°C. The reactors were gently shaken by hand every day. Each day 1 mL gas sample was obtained from each reactor using Hamilton® gas syringes over a period of 25 days. The samples were injected to a gas chromatographer (Thermo Finnigan Trace GC) equipped with a flame ionisation detector.

6.4. RESULTS

Since the start of operation all the studied plants have generally been achieved acceptable levels of treatment, according to data from bimonthly grab samples taken by the company in charge of operation and maintenance (Table 6.2). Taking into account all available data, mean TSS removal rates range from 85% (Alfés) to 91% (Verdú), BOD₅ from 86% (Almatret south) to 93% (Verdú), and COD removal rates range from 80% (Almatret south) to 87% (Verdú). Thus, the overall pollutant-removal efficiencies of these plants demonstrate that the combination of horizontal SSF CWs and maturation ponds may be effective and reliable for TSS and organic matter removal.

Contribution of the different unit processes to pollutant removal

Figure 6.6 illustrates the average of the total and COD fractions in the influent and effluent of each unit process of the five plants. During this study, the average total COD removal efficiencies of the systems ranged from 78 to 93% and most total COD effluent concentrations were under the 125 mg/L limit of the European Union (Council Directive 91/271/EEC). More precisely, only the Almatret north system had effluents with COD concentrations above this requirement. The influent COD concentration was clearly lower in Verdú (224 mg/L) than in the other systems (>500 mg/L). This was due to potable water infiltrations into the sewer system that dilute pollutant concentrations.

Table 6.2 Average, standard deviation (in brackets) and efficiency removal of TSS, DBO₅ and COD (mg/L) of each system after three years of operation. n= 34

Caon Syste	in alter th	TS		tion. n= 34.	DB	O ₅	D 1	000	<i>(</i>	D 1
Systems	Years	(mg		Removal	(mg		Removal	COD	(mg/L)	Removal
,		Inf	Éff	(%)	Inf	Eff	(%)	Inf	Eff	(%)
	2003	200	10	95	120	5	96	272	37	86
	2003	(139)	(8)	(5)	(77)	(2)	(12)	(138)	(15)	(9)
Verdú	2004	153	19	88	88	9	90	164	24	85
Veruu	2004	(60)	(11)	(5)	(29)	(5)	(3)	(35)	(14)	(5)
	2005	250	22	91	225	16	93	449	35	92
	2005	(342)	(20)	(21)	(192)	(12)	(11)	(288)	(32)	(12)
	0000	237	16	93	120	10	92	293	43	85
	2003	(269)	(10)	(4)	(66)	(6)	(3)	(229)	(13)	(13)
Alfés	2004	253	30	88	94	10	90	368	41	89
7 11100	2004	(61)	(6)	(1)	(25)	(5)	(4)	(220)	(9)	(3)
	2005	167	45	73	286	23	92	514	68	87
	2005	(38)	(50)	(29)	(130)	(12)	(8)	(224)	(36)	(5)
	2003	194	32	84	156	19	88	378	67	82
	2000	(42)	(9)	(12)	(57)	(13)	(9)	(115)	(23)	(6)
Corbins	2004	278	23	92	162	13	92	298	51	83
COIDIIIO	2001	(238)	(12)	(4)	(107)	(8)	(3)	(153)	(90)	(8) 86
	2005	183	16	91	252	25	90	480	65	
		(158)	(11)	(13)	(86)	(13)	(10)	(126)	(33)	(12)
	2003	238	24	90	153	17	89	400	81	80
Λ I L L		(138)	(10)	(5)	(104)	(13)	(5)	(163)	(35)	(6)
Almatret	2004	289	44	85 (6)	100	11	89	197	32	84
north		(77) 212	(18) 20	(6) 88	(12) 332	(2) 26	(2) 86	(26) 601	(4) 75	(2) 82
	2005		(21)		332 (265)		(14)	(485)	(48)	
		(222) 312	44	(6) 86	177	(13) 17	90	494	96	(15) 80
	2003	(297)	(31)	(5)	(94)	(9)	(4)	(273)	(35)	(6)
Almatret		350	46	86	123	15	88	252	32	(o) 87
south	2004	(135)	(19)	(6)	(26)	(4)	(4)	(93)	(15)	
South		114	15	87	201	29	85	384	95	(2) 75
	2005	(48)	(10)	(9)	(150)	(14)	(11)	(212)	(57)	(19)

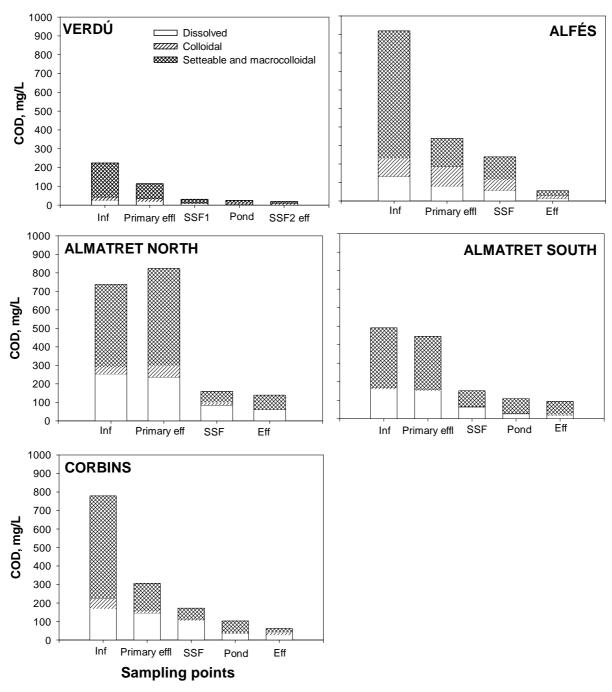


Figure 6.6 Averages of the total COD and the considered fractions (setteable and macrocolloidal: >1.2 μ m, colloidal: 0.2-1.2 μ m, and dissolved: < 0.2 μ m) in the influent and the effluent of each unit process of the five plants evaluated. n = 3 in each sampling point.

Approximately 50-60% of the total influent COD was removed in the primary treatment, except in the two Almatret plants, where the COD concentrations were similar before and after the septic tank. In general, most of the influent COD was due to settleable and macrocolloidal particles (60-80%), and most of this COD was already removed with the primary treatment (56-88%). In the final effluent, the settleable and macrocolloidal COD still made up an important part of the total COD (32-74%), especially in systems where the final treatment unit is not a CW, as in Alfés, Almatret north and Almatret south.

In contrast to the generally high overall COD removal efficiencies observed in the treatment plants, the mean ammonium removal was low (0-43%) (data not shown). Only the two Almatret plants had ammonium removal efficiencies greater than 50%. Ammonium concentration stayed quite constant throughout the various unit processes in the systems with the lower removal efficiencies (Verdú, Alfés and Corbins).

Total COD removal in the CWs ranged from 24% (Verdú 2, which receives the effluent of a pond) to 81% (Almatret north, where the primary treatment was not working properly). The total COD concentration in the effluent of the CWs was greater than 150 mg/L, except at Verdú. Furthermore, ammonium removal efficiencies were low in general and, in the SSF CWs of Verdú and Alfés, there was actually no ammonium nitrogen removal (Table 6.3)

Table 6.3 Mean concentrations, standard deviations (in brackets) and mean removal efficiencies of the COD and ammonium of the evaluated horizontal SSF CWs. n = 3

	Т	otal COD (mg/L)	NH ₃ -N (mg/L)			
SSF CWs	Influent ¹	Effluent ²	Removal (%)	Influent ¹	Effluent ²	Removal (%)	
Verdú 1	114 (71)	31 (18)	73	6 (1)	7 (1)	-	
Verdú 2	25 (8)	19 (8)	24	7 (1)	6 (3)	14	
Alfés	379 (192)	233 (161)	38	34 (23)	34 (8)	-	
Corbins	306 (71)	173 (53)	43	36 (17)	27 (8)	25	
Almatret north	823 (314)	159 (2)	81	58 (17)	49 (14)	16	
Almatret south	444 (168)	151 (98)	66	42 (7)	35 (15)	17	

¹ This is in fact the primary effluent, with the exception of Verdú 2 that is pond effluent.

With respect to the removal of the various COD fractions considered in this study, the SSF CWs reduced the settleable and macrocolloidal COD by more than 50%, except at Alfés and Verdú 2 (Table 6.4). In general, the colloidal and dissolved COD fractions were reduced less than the settleable and macrocolloidal fractions.

² Effluent of the evaluated horizontal SSF CWs.

Table 6.4 Mean removal efficiencies (%) of the different COD fractions in the different SSF CWs evaluated.

SSF CW	Setteable and macrocolloidal (>1.2 µm)	Colloidal (0.2-1.2 µm)	Dissolved (< 0.2 µm)
Verdú 1	78	68	52
Verdú 2	33	20	_1
Alfés	39	45	33
Corbins	58	10	28
Almatret north	88	73	64
Almatret south	69	71	58

⁻¹ No net removal.

Solids accumulation and hydraulic conductivity

There was a much greater amount of accumulated interstitial solids (99%) than solids adhered to gravel (<1%) in all of the SSF CWs. As expected, most solids accumulated near the inlet, but in some cases the distribution was heterogeneous (Figure 6.7). In the Corbins SSF CW, where the greatest solids accumulations were observed (11-57 kg/m2), most of the solids in the inlet accumulated near the middle of the wetland. This trend was also observed in Alfés (3-35 kg/m2). In Almatret south (3-20 kg/m2), however, the greatest accumulations occurred on one side of the wetland. At Verdú 1 (3-13 kg/m2), Verdú 2 (2-12 kg/m2) and Almatret north (2-10 kg/m2), the inlet solids accumulation was rather homogeneous. Significant spatial variations in solids accumulation in the inlet zone of the SSF CWs may be related to a non-homogeneous distribution of influent water.

Although we expected that the accumulated solids (interstitial and adhered) would have high organic matter content, the results indicated that the organic fraction, expressed as a percentage of VSS/TSS, ranged from 10 to 20% in most cases. The only exception was Verdú 2, where the organic fraction was around 75% in all cases. Again, this is related to the pond influent, in which large microalgae populations were observed.

The hydraulic conductivity (K) was clearly lower in the inlet zone than the outlet zone. Generally, it was negatively correlated with the solids content of the CW in the same zone (Figure 6.8). In fact, with the exception of wetland Verdú 2, in all the rest of CW at least one of the K values observed near the inlet was below 3.0 m/d. These low hydraulic conductivities near the inlet are consistent with the ponding observed in the field in all of the SSF CWs analysed.

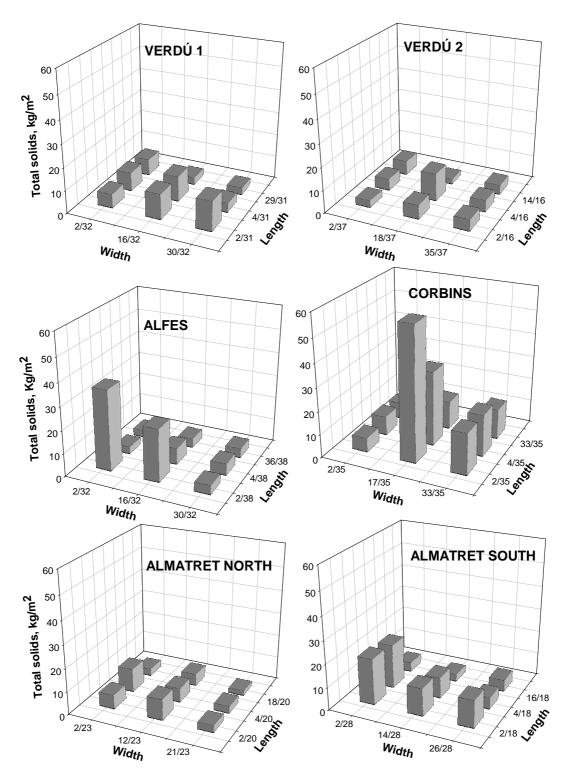


Figure 6.7 Total solids accumulated in the sampling points of the evaluated SSF CWs. Note that in all wetlands the two first stretches were placed at 2 and 4 m from the inlet, and the third at 2 m from the outlet. For clarity the width and the length are represented in fractional terms.

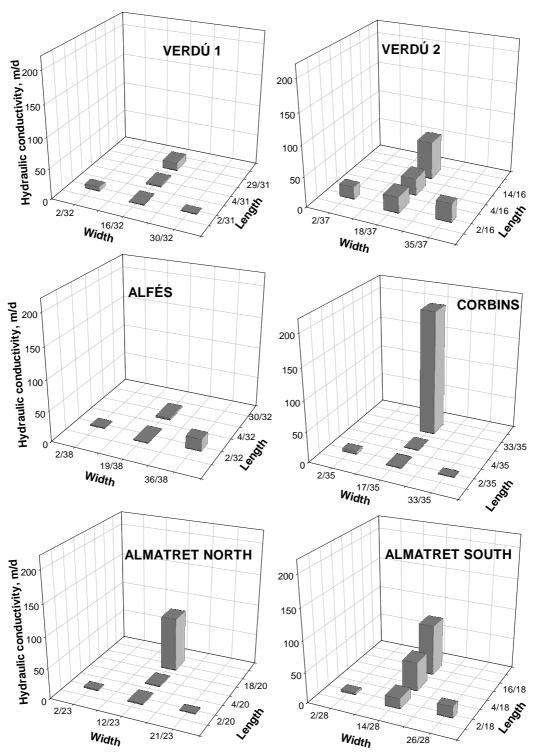


Figure 6.8 Hydraulic conductivity in the sampling points of the SSF CWs. Note that in all wetlands the two first stretches are placed at 2 and 4 m from the inlet, and the third at 2 m from the outlet. For clarity the width and the length are represented in fractional terms.

Biodegradability tests

Figure 6.9 shows the results of the aerobic and anaerobic tests. All of these tests were conducted at the same time, using samples of the same origin. Initial VSS values were approximately 5000 mg/L in Alfés and 3000 mg/L in Verdú.

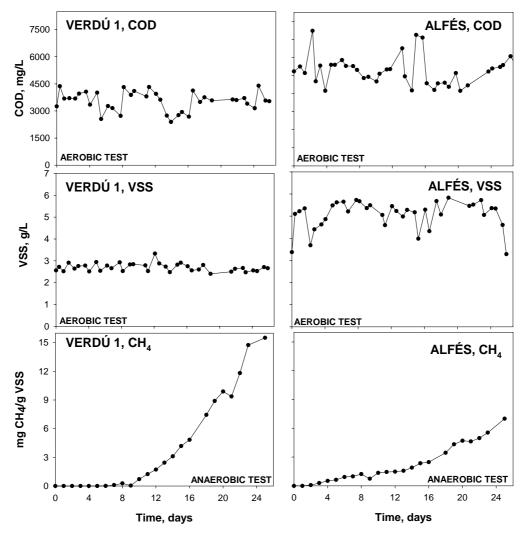


Figure 6.9 Changes in time of the COD and VSS concentrations in the aerobic tests and of accumulated methane concentration in the anaerobic tests (20 °C) conducted with samples from the SSF CWs Verdú 1 and Alfés.

In the aerobic tests, the organic matter content in terms of COD or VSS was quite constant throughout the testing period. In the anaerobic tests at 5°C, the microbial activity was very low and almost no methane accumulated in the headspace at the end of the experiments (data not shown). At 20°C, anaerobic microbial activity was clearly detected by the increasing methane accumulation in the headspace of the reactors.

Nevertheless, the specific activity rates (4 and 2 mg CH₄/g VSS.day for Verdú 1 and Alfés respectively) were very low compared with other types of sludge. The results of the biodegradability tests indicate that the organic matter accumulated in the wetlands is recalcitrant.

6.5. DISCUSSION

The urban wastewater treatment plants evaluated in this study generally produce effluents with a COD concentration below 100 mg/L. Therefore, they meet the European COD discharge requirement of 125 mg/L. Thus, horizontal SSF CWs combined in series with ponds appear to be a robust alternative for the sanitation of small rural communities, at least in terms of COD. Ammonium removal in these plants was low, ranging from 18 to 54% (except for Verdú, where there was no removal). However, these values are within the range reported for systems of this type (Vymazal, 1999).

The percentages of the influent COD fractions observed in this study were 60-80% for settleable and macrocolloidal (>1.2 μ m), 2-11% for colloidal (0.2-1.2 μ m) and 12-34% for dissolved (<0.2 μ m). These proportions are not very different from those of the municipal wastewaters evaluated by Marani et al. (2004), who found 34-49% for >1 μ m, 3-10% for 0.2-1 μ m and 13-28% for <0.2 μ m. In all of the evaluated plants, the removal of the settleable and macrocolloidal fraction made up the largest part of the total COD removal (60 to 80%) and the colloidal and dissolved fractions made up the smallest part (2 to 34%). In all of the plants, primary treatment played a very important role in the removal of the settleable and macrocolloidal COD fraction (56 to 83%), except in the two Almatret systems, where an excess of sludge accumulation in the septic tanks negatively influenced the removal efficiency of the settleable and macrocolloidal COD fractions. This demonstrates the importance of primary treatment in natural wastewater systems, as was pointed out by Tchobanoglous (2003). All efforts devoted to improve primary treatment will result in better overall efficiency and reduce the solids accumulation rates and consequent clogging of wetlands.

On the other hand, the effluent COD concentrations of the horizontal SSF CW units (except for the Verdú wetlands) exceed the European COD standard (Table 6.3). They are also higher than previously reported COD concentrations for SSF CWs that have been operating for a similar length of time (Dahab and Surampalli, 2001, Vymazal, 2002 and García et al., 2005). Table 6.5 shows that most SSF CWs studied receive organic loads close to those described as the limit for SSF CWs. According to USEPA (2000), the limit is 6 g BOD₅/m².d or 8.4 g COD/m².d, considering that in municipal wastewater COD is 1.4 times BOD₅

(Metcalf & Eddy, 2003). The low ammonium removal efficiency in the SSF CWs (Table 6.2) could also be related to these high loads and the fact that the samples were taken in the winter, when low temperatures are the key limiting factor for major ammonium removal mechanisms such as nitrification (Kadlec et al., 2000).

Table 6.5 Organic matter surface loading rate, accumulated solids, percentage of volatile solids and accumulation rates in different SSF CWs.

		Type of SSF CW	Surface loading rate (gCOD/m².d)	Surface loading rate (gTSS/m².d)	Accumulated solids (kg/m²)	VSS/TSS (%)	Solids accumulation rate (kg/m².year)
Tanne Sukias	r and s (1995)	Horizontal	-	2.2 – 7.3	1.9 – 6.5	82	1.5 – 4.5
Tanne (1998)	r et al.,	Horizontal	-	2.2 - 7.3	8.5 – 18.6	80	1.3 – 3.0
,	renc and	Vertical Vertical	a67.2 a89.6	-	69.7 – 90.9 26.9 – 52.7	35 25	8.7 – 11.3 8.9 – 17.5
	(2005)	Vertical	a44.8	-	14.7 – 50.9	50	3.6 - 12.7
	Verdú 1 Verdú 2 Alfés	Horizontal Horizontal Horizontal	b3.8 - 10.4 b3.1 - 8.5 b5.3 - 9.2	2.8 – 4.5 - 3.2 – 4.9	2.8 – 12.8 2.3 – 11.9 2.6 – 35.1	10 – 39 11 – 89 7 – 13	1.0 – 1.7 - 1.2 – 1.8
This	Corbins	Horizontal	b10.9 - 17.5	6.5 - 10.0	11.1 – 57.3	3 – 19	2.4 - 3.6
study	Almatret north	Horizontal	b4.5 - 13.8	4.5 - 6.2	2.3 - 9.6	5 – 30	1.7 – 2.3
	Almatret south	Horizontal	⁶ 6.2 – 12.9	2.6 - 8.0	2.8 – 20.3	5 – 28	0.9 - 2.7

^a Surface loading rate was calculated according with relation COD/DBO = 1.4

With respect to the removal of the various COD fractions in the SSF CWs (Table 6.4), removal rates were higher for the settleable and macrocolloidal COD fractions than for the other studied fractions (colloidal and dissolved COD). Specifically, settleable and macrocolloidal COD removal ranged from 33 to 88%, colloidal COD removal ranged from 10 to 73% and dissolved COD removal ranged from 28 to 68%). This behaviour seems rather logical because one the main means of organic matter removal in a SSF CW is the retention of physical particles in the bed. Furthermore, our results are consistent with those of Puigagut et al. (2006), who found that most effluent COD found in SSF CW was dissolved COD.

The TSS loading rates applied to the wetlands over the three-year period ranged from 2.6 to 10 g TSS/m².d (Table 6.5). These loading rates are somewhat higher than those reported by Tanner et al. (1998) (2.2-7.3 g TSS/m².d). In particular, the high mean TSS loading rates recorded for Almatret north, Almatret south and

^b Surface loading rate for COD was calculated considering a reduction of primary treatment obtained in this study and for TSS was calculated considering a mean reduction of 60% of the primary treatment

Corbins (5.4, 5.7 and 7.8 g TSS/m².d respectively) were consistent with the high solids accumulation rate in these SSF CWs (Table 6.5). The wetlands with lower solids accumulation rates (the two Verdú systems) also operate with lower loading rates. Despite this, the accumulation rates observed in all CWs analysed are similar to those reported by Tanner and Sukias (1995) and Tanner et al. (1998) for horizontal SSF CWs treating farm dairy wastewater. Table 6.5 also shows that the vertical SSF CW systems, which have the highest surface organic loading rates of all the systems described in the reviewed literature, also have the highest solids accumulation rate. The results of our study, when compared with those of other studies, demonstrate that solids accumulation rates depend to a greater extent on both COD and solids load.

On the other hand, the relative importance of VSS respect of the total accumulated solids is lower when compared with that found by Tanner and Sukias (1995) and Tanner et al. (1998). Our study indicated that only 20% of the accumulated solids were organic. This low proportion of VSS/TSS could be related to a greater degree of mineralization of the organic matter of our samples, which were taken from quite deep in the CW (20-30 cm of depth). This hypothesis is supported by the results of Nguyen (2000), Langergraber et al. (2003) and Chazarenc and Merlin (2005), who report that the degree of organic matter mineralization increases with depth. Another factor that may contribute to the large amount of inert solids found in this study is the presence of fine particles, silt and clay coming from the gravel media. This phenomenon is especially evident in the Alfés and Corbins plants, where new gravel media was added by the management company to cover the ponds near the inlet of the SSF CWs (Table 6.5).

Concerning the characteristics of accumulated solids in the granular medium, the organic matter retained in the inlet zone of the SSF CWs in Alfés and Verdú was very stable and difficult to biodegrade under both aerobic and anaerobic conditions. Using olive-mill effluents, Fakharedine et al. (2006) conducted an aerobic degradation experiment very similar to the one performed in this study and found a COD removal of 80% within 20 days. In our case, within a similar period of time, the COD concentration remained almost constant and therefore the removal was very low (less than 10%). Moreover, based on the anaerobic tests, we estimated the anaerobic-specific activity at 0.001-0.002 gCOD_{CH4}/gVSS.d, which is clearly lower than that reported for primary sludge and aerobic ponds and closer to that reported for the recalcitrant compounds found in fresh dung and river mud (Field et al., 1988). This low anaerobic-specific activity could be explained by the large amount of refractory material found in the accumulated solids in CWs, which are described as mainly lignocellulose and humic-type substances (Tanner and Sukias, 1995 and Nguyen, 2001).

The main consequence of solids accumulation in SSF CWs is a reduction either the hydraulic retention time (Tanner and Sukias, 1995) and the hydraulic conductivity (K) (Watson and Choate, 2001). In our studies, K ranged from 0 to 30 and from 12 to 217 m/d in the inlet and outlet zones respectively in the CWs analysed (Figure 8). These K values, though lower than those reported by Watson and Choate (2001) (340 m/d and 8,400 m/d in the inlet and outlet zones respectively), follow the same trend, that is, lower values at the inlet than at the outlet. Moreover, our results show that hydraulic conductivity is negatively correlated with solids accumulation in almost all of the CWs analysed (Figure 6.7). The only exceptions are the two Almatret systems. This exception might be due to the phenomena already described by Tanner et al. (1998), who did not find a clear relationship between the hydraulic residence time and solids accumulation. In our case, as Tanner et al. (1998) described for the hydraulic retention time, hydraulic conductivity could also be affected by the presence of solids and by their distribution pattern, composition and degree of compactation. Moreover, the heterogeneous distribution of solids observed in the inlet zone of several of the SSF CWs studied (Figure 6.7) may be related mainly to an irregular distribution of the wastewater across the width of the wetland. Thus, to minimise problems related to heterogeneous solids accumulation, wastewater distribution systems should be designed and built to ensure good distribution across the entire width of the wetland.

6.6. CONCLUSIONS

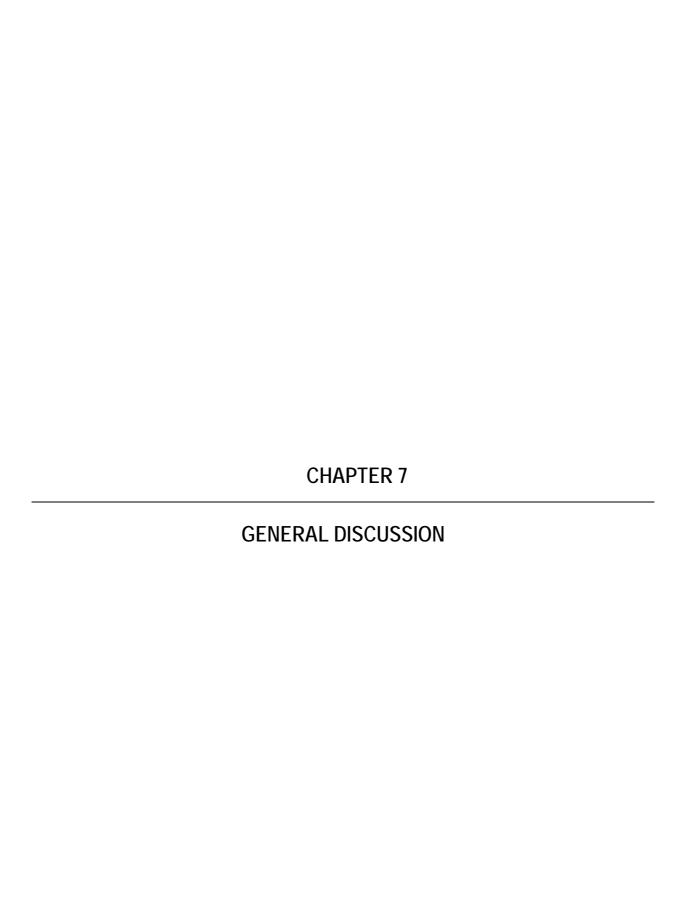
The amount of soils accumulated during the 3 or 4 years that the studied systems had been operating ranged from 2.3 to 57 kg/m². The two SSF CWs at Verdú had in general the lowest solids accumulation (2.3-13 kg/m²) and the lower organic loading rate (3.1-10 gCOD/m².d). The SSF CW at Corbins had the highest solids accumulation (11-57 kg/m²) and the highest loading rate (11-17 gCOD/m².d). Thus, the results of this study clearly show that there is a positive relationship between the amount of accumulated solids and the organic loading rate.

The amount of organic matter in the accumulated solids was usually quite low (<20%). Only the Verdú 2 SSF CW had solids with a high percentage of organic matter (>75%), because it received pond effluent. The low organic matter content observed in most of the systems may be related to a high degree of mineralization of the organic matter and the presence of mineral particles from the granular media. The aerobic and anaerobic biodegradability tests conducted on the organic matter accumulated in the gravel of the Alfés and Verdú SSF CWs indicated that the accumulated organic matter is very recalcitrant and cannot be easily biodegraded.

The most-reduced COD fraction was the settleable and macrocolloidal COD in the majority of the SSF CWs. This is therefore the fraction most closely related to solids accumulation in the systems we studied.

Lower hydraulic conductivity values were observed near the inlet of the SSF CW (0-4 m/d), where solids accumulation was also greater. At the outlet, hydraulic conductivity was higher (12-200 m/d). However, this inverse relationship between hydraulic conductivity and accumulated solids is not direct, due to the heterogeneous distribution patterns, composition and degree of compaction of the solids.

Practical recommendations derived from this study that can prevent or reduce clogging in horizontal SSF CWs are: 1) design systems with the lowest possible organic loading rate, since there is a positive relationship between loading rates and solids accumulation rates, 2) consider using advanced primary treatment systems such as filter screens or high-rate clarification, which could considerably reduce the surface loading rate and 3) ensure that the wastewater is distributed across the entire width of the systems to avoid heterogeneous distribution of solids, which causes short-circuiting and dead zones.



7.1. GENERAL DISCUSSION

The principal goal of this dissertation was to investigate the impact of organic matter types (dissolved vs. particulate), on the treatment efficiency of horizontal SSF CW. Experiments were conducted using either synthetic or urban municipal wastewater. Parameters of interest included removal rates of organic matter (COD) and ammonium nitrogen. Studies were also conducted in experimental- and full-scale SSF CW to evaluate the impacts of organic matter accumulation on hydraulic conductivity. Specifically, experiments were designed to evaluate the impacts of: 1) the form of organic matter (dissolved and readily biodegradable vs. particulate and slowly biodegradable) 2) the organic matter loading rates (low to high), 3) the use of a physico-chemical pretreatment to enhance removal of suspended solids prior to treatment in experimental SSF CW systems, 4) the effect of the hydraulic regime (intermittent or continuous feeding), and 5) the solids accumulation on hydraulic conductivity and wastewater treatment in experimental and full-scale wetland systems. The following sections provide a brief description of individual experiments followed by pertinent discussions of the results.

Effect of dissolved vs. particulate organic matter on wastewater treatment

Two experiments were conducted over a period of nine and four months respectively to evaluate the impact of dissolved versus particulate organic matter on treatment efficiency in SSF CW. Both studies were conducted in small plastic containers of 0,54 m² (0.35 m deep), that were designed to simulate the conditions of a shallow SSF CW. These experimental systems were fed with synthetic wastewaters containing either glucose (readily biodegradable), or particulate starch (slowly biodegradable). The results from the first ninemonth study demonstrated that at low organic loading rates (5-6 g COD/m².d), COD removal averaged greater than 80% and was similar for both the dissolved (glucose) and particulate (starch), forms of organic matter. Removed efficiency with respect to ammonium-N was near 50% in both systems. However, ammonium–N removal was slightly higher (45 vs 40%), in the glucose-fed SSF CW. It is surmised that the greater removal of ammonium-N was probably related to the greater heterotrophic microbial growth that occurred in the glucose-fed system

Effect of high loading rates of dissolved vs. particulate organic matter on treatment efficiency in SSF CW

The results from the nine-month study clearly demonstrated that in lightly loaded SSF CW, there were no differences between soluble and particulate carbon sources with respect to COD removal efficiency. However, we hypothesized that if the systems had been loaded at higher organic loading rates, the treatment differences between dissolved and particulate organic matter would have become apparent in a relatively short period of time. Therefore, a four month follow-up study was conducted in which the organic loading rate to each system was increased notably (5-6 g COD/m².d to. 20-22 g COD/m².d). Results of this study revealed that even under conditions of significantly higher organic loading rates, the COD removal efficiency for both systems was similar. Thus, after 13 months of operation, including 9 months of low organic loading (Caselles-Osorio and García, 2006a), and 4 month of high organic loading, both SSF CW provided similar levels of COD removal under a wide range of operating conditions. In summary, the overall COD removal rates for glucose- and starch-fed systems were very similar (P>0.05), ranging from 85 to 95%. Lack of differences occurred even after the organic loading rate was increased. Thus, it is clear from these results that the organic matter removal efficiency of SSF CW is not sensitive to the type of organic matter with which they are fed (whether dissolved or particulated) under a wide range of loads.

Effect of pyhisico-chemical pre-treatment on effluent water quality from experimental SSF CW

An eight month study was conducted in shallow replicate experimental SSF CW units (see previous study for design details), to evaluate the effect of a physico-chemical pretreatment on effluent water quality. One of the systems was fed with settled urban wastewater (control), while the other system was fed with settled urban wastewater that was also subjected to a physical-chemical pretreatment. The physical chemical pretreatment consisted of amending the settled wastewater with 70 mg/L of Tanfloc SG, a cationic polymer used to enhance coagulation and flocculation. The study revealed that the physico-chemical pretreatment was successful in removing up to 50% of the influent COD as compared to the control. However, the use of the physico-chemical treatment did not significantly improve the quality of the SSF CW effluent in terms effluent concentrations of COD and ammonium-N (P>0.05). The efficiency of COD elimination was around 85%, whereas the ammonium elimination was unusually high, ranging from 80 to 90%. After 8 months of operation the SSF CW fed with settled wastewater had a lower hydraulic conductivity than the SSF CW fed with the physico-chemically treated wastewater. This indicates that the physico-chemical pretreatment may have helped to control sediment buildup, and thereby helped to extend the useful life of the SSF CW.

Effects of continuous and intermittent feeding on treatment efficiency of SSF CWs

In previous studies conducted by Caselles-Osorio and Garcia (2006b), it was noted that intermittently-fed SSF CW systems provided exceptionally high removal of COD and ammonium-N. In order to better understand these high removal rates, a subsequent study was conducted to compare pollutant removal dynamics in SSF CW using intermittent or continuous feeding regimes. The main conclusion of this investigation was that intermittent feeding in shallow SSF CW provided a more oxidized treatment environment in comparison to continuous feeding. This in turn promoted a greater removal of ammonium-N in the intermittently fed system (80-99%) as compared to the continuously fed system (71-85%). In addition, it was observed that SSF CW with high aboveground macrophytes biomass had a more oxidized root zone than systems with low plant biomass. The system with high biomass (and a more oxidized root zone), had COD and ammonium-N removal rates of 81 and 98% respectively as compared to low biomass systems which had removal rates of 73 and 72% respectively.

Solids accumulation in full-scale subsurface flow constructed wetlands

This study was conducted to survey six full-scale SSF CWs and to quantify the amount of accumulated solids in the granular (gravel) medium. This data was used to examine the relationships between solids accumulation, treatment efficacy and hydraulic conductivity. Laboratory-scale testes were also conducted to determine aerobic and anaerobic biodegradability of accumulated organic matter from two of the SSF CW. The results showed a positive relationship between organic loading rates and the amount of accumulated solids in SSF CW. Organic matter content, expressed as a percent of the accumulated solids, was quite low and generally less than 20%. The most-reduced COD fraction was the settleable and macro-colloidal COD. This is therefore the fraction most closely related to solids accumulation in the systems we studied. Lower hydraulic conductivity values were observed near the inlet of the SSF CW, where solids accumulation was also greater. At the outlet, solids accumulation was much lower and hydraulic conductivity was higher.

Characteristics of organic matter (dissolved vs. particulate), and their impacts on treatment efficiency

Urban municipal wastewater contains different amounts of dissolved and particulate organic matter, with COD concentrations ranging from 250 to 1000 mg/L (Metcalf & Eddy, 2003). Many organic constituents are readily biodegradable, such as glucose, while others are more slowly biodegradable, like starch. In SSF CWs, the dissolved organic fraction is removed by microbial biofilms that growth on the surfaces of the

granular matrix and the roots or aquatic macrophytes (Burgoon et al, 1995). Particulate organic matter is also removed, by rapid sedimentation, filtration, adsorption and biofilm entrapment. Subsequently, the labile fraction is mineralized and oxidized by microbial action, and the residual matter (refractory organics and mineral matter), is stored in the interstitial pores of the substrate (Kadlec et al., 2000). Analyses of the above noted experiments revealed that SSF CWs were very effective at removing COD, irrespective of organic matter loading rate or form of organic matter (dissolved vs. particulate). In paired comparisons of various treatments, COD removal rates for dissolved (glucose) and particulate (starch), organic matter were very similar, and the same trends were observed in wastewater with or without physico-chemical pre-treatments. These results are not consistent with results reported for conventional wastewater treatment systems, where the particle-size distribution of organic matter significantly affects the efficiency of COD removal (Levine et al., 1991; Sophonsiri and Mongenroth, 2004). The high and consistent removal of COD in SSF CWs is commonly cited, and is related to the high specific surface area of the granular matrix, long HRT's, rapid sedimentation, filtration, biofilm entrapment, and efficient microbial oxidation of organic matter under either aerobic or anaerobic conditions (Kadlec et al., 2000, USEPA, 2000).

It should be noted that the results reported in this dissertation are based on a series of experiments that were conducted over relatively short time periods (months), and in relatively new treatment systems. The experiments were designed to evaluate the impact(s) of organic matter type and loading rates on efficiency of SSF CW. The first two experiments tested different organic matter types (dissolved vs. particulate), and lasted for a total of 13 months. Subsequently, an 8 month study was conducted to evaluate primary settling and the use of a physico-chemical treatment. This should be taken into account because treatment efficiency can change with time, especially in highly loaded systems in which there can be excessive accumulation of organic solids and mineral matter in the inlet zone. Over the course of time, the interstitial pore spaces of the granular matrix will fill with biofilm, dead bacterial cells, plant detritus, and mineral matter from chemical precipitation and decomposition (Langergraber et al., 2003). This accumulation of sediments reduces porosity, diminishes the hydraulic retention time, induces short circuiting and promotes surfacing of wastewater (ponding) (Tanner et al., 1998; Langergraber et al., 2003). For example, Tanner et al., (1998) in farm dairy wastewater observed that the retention of suspended solids was higher during the first years of system operation, but that retention rates diminished significantly over a period of five years.

In general, COD removal rates in the experimental SSF CW were relatively high and very stable during all of the studies, irrespective of treatment environments. The reason for such high and stable removal rates over a wide range of treatment environments can be explained on the basis that organic matter can be readily oxidized in aerobic, anoxic and anaerobic environments. However, in contrast to COD, removal of ammonium-N was variable and highly sensitive to treatment environments. It is well documented that the major removal pathways for nitrogen in treatment wetlands is nitrification followed by denitrification (Kadlec and Knight, 1996). Furthermore, nitrification requires an oxidized environment for the microbial transformation of ammonium-N to nitrate. In a preliminary experiment, the SSF CW systems were fed with synthetic wastewater, both at low and high organic loading rates. The system that received dissolved organic matter (glucose), had an average ammonium-N removal rate of near 50%. However, the system that received particulate organic matter (starch), removed only 42 % of the ammonium-N. It is surmised that this difference may have been due to major assimilation of ammonium-N by heterotrophic bacteria that grew rapidly in the presence of soluble and readily oxidized glucose substrate. These relatively low ammonium removal rates in this experiment (42-50%), may have also been influenced by low plant biomass, as the growth of plants was less than that observed in the field, and the reed stems were thinner and shorter. Had plant growth been more robust, it is proposed that more ammonium-N would have been assimilated by the plants. (It should be noted that this experiment was conducted inside a building and that the plants were exposed to natural light and Gro-lux lamps).

In a subsequent study designed to evaluate a physico-chemical pretreatment for removing suspended solids, ammonium-N removal rates were exceptionally high, averaging 80 to 90%. These high removal were not due to the treatment *per se*, as there was no difference between the physico-chemical treatment and the control (P>0.05). The high levels of removal were due to the cumulative effects of shallow bed depth, intermittent feeding, and high plant biomass (it should be noted that these experimental units were located on the roof of the Engineering building and that the plants were exposed to full sunlight). In previous studies Garcia et al. (2004a), demonstrated that shallow beds had a more oxidized root zone and higher ammonium-N removal rates than deep beds. Furthermore, in subsequent tests we demonstrated that intermittent feeding in the presence of high plant biomass also promoted an oxidized root zones and enhanced removal of ammonium-N. Thus, the fortuitous combination of shallow beds, intermittent feeding and high plant biomass provided the oxidized root zone required for nitrification; and the high plant biomass would have also assimilated a portion of the ammonium-N.

Effect of the organic matter (dissolved vs. particulate) on hydraulic conductivity (k) in SSF CW

Although we did not conduct exhaustive studies related to hydraulic conductivity (k), in SSF CW, it is well known that chronic accumulation in the zone of entrance can effect porosity, conductivity, short-circuiting,

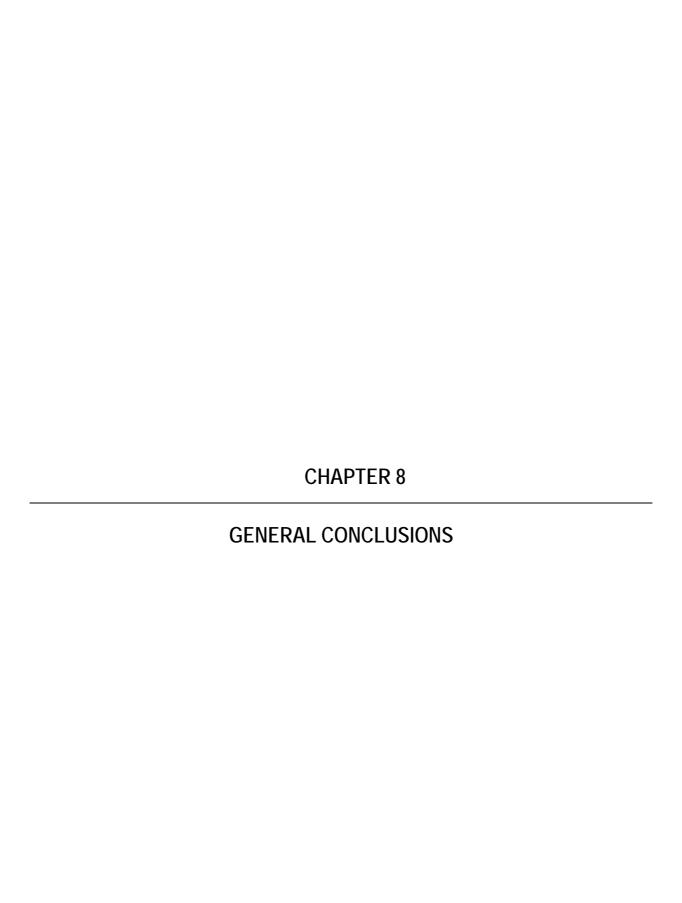
surface ponding of the wastewater, odors, presence of insects and potential reductions in treatment efficiency (Platzer and Mauch, 1997). However even in short duration studies (months), in experimental SSF CW it was possible to measure marginal differences in K in systems fed with glucose, a highly biodegradable organic substrate, as opposed to starch, a slowly biodegradable substrate. It is surmised that these small differences in K may have been due to treatment-related growth of biofilm which would have diminished pore volume, increased frictional loss, and reduced K. Significant differences in K were also observed in the use of a physico-chemical pretreatment to remove suspended solids in the influent wastewater. This pretreatment successfully removed suspended solids by 50%, which in turn diminished the accumulation of solids in the zone of entrance. In the SSF CW with physico-chemical pretreatment, K values were greater than those measured in the control (primary settling but no physico-chemical pretreatment). Also, solids accumulation studies conducted in several large-scale SSF CWs indicated that systems receiving high organic loading rates had significantly reduced K values in the zone of entrance.

Control of organic matter accumulation though use of physico-chemical pretreatment.

A major problem in SSF CW is the pervasive accumulation of organic matter in the zone of entrance. This accumulation over time contributes to pores blockage and changes in the hydrodynamic behavior of the system. Under worst case scenarios, the life-span of the wetland treatment system can be reduced to a few years. In this study it was demonstrated that a physico-chemical pretreatment of the influent wastewater removed up to 50% of the suspended solids and thus significantly reduced the amount of solids accumulation in the zone of entrance. This was correlated with less clogging and a relatively high K value. In accordance with these results, it is proposed that physico-chemical pretreatments could be used to lengthen the useful life of SSF CWs. To underscore this point, García et al. (2006) applied a dynamic model to evaluate the use of physico-chemical pretreatments to reduce the risk of clogging in SSF CW. Tests were conducted to validate the model and results showed that after 120 days of operation, porosity decreased 17% in SSF CW without physico-chemical pre-treatment, but only 6% in SSF CW with the pre-treatment. The use of a prior physico-chemical treatment is therefore a good alternative for avoiding an anticipated clogging of SSF. This is especially true if the disadvantages of the physico-chemical treatments (extra cost for chemical and more sludge) are, in addition, compensated with for example phosphorus removal. Recently, costs have become very competitive with respect to the application of physico-chemical pretreatments (Tchobanoglous et al., 2003).

Shallow SSF CW and intermittent feeding regimes

Careful review of data from the physico-chemical pretreatment study revealed that ammonium-N removal rates often surpassed 80%, and these high removal rates were not due to either of the two treatments under evaluation. These are unusually high rates of ammonium-N removal in SSF CWs. In fact, most of the literature, including US EPA (2000), recommends use of SSF CW principally for the elimination of TSS and COD. These same literature citations point out the poor performance of SSF CW with respect to ammonium-N removal. Therefore, it was hypothesized that such high ammonium-N removal rates could be explained by the concurrent use of shallow SSF CW (Garcia et al., 2004), and intermittent feeding. Thus additional experiments were conducted to test this hypothesis. Study results confirmed that the concurrent use of shallow beds (0.25 – 0.3 m depth), and intermittent feeding promoted a more oxidized environment and allowed for ammonium-N removal rates ranging from 80-90%.



8.1. GENERAL CONCLUSIONS

- 1. The type of organic matter, either dissolved (glucose) or particulate (starch), did not affect the efficiency of COD removal in the SSF CW. Several experiments were carried out with synthetic wastewater that was amended with either starch (slowly biodegradable) or glucose (rapidly biodegradable). After 8 months of operation, the COD removal results indicated that the SSF CWs were not sensitive to the type of organic matter. Average COD removal rates for glucose ranged from 76 to 94%, while values for starch were 70 to 94%. Furthermore, COD removals for both forms of organic matter were not affected by hydraulic retention time or sulfate concentrations. The removal of ammonium-N was modest for both forms of organic matter, but was slightly greater in the wetland fed with glucose (29 to 57%) as compared to starch (20 to 53%). The hydraulic conductivity in the zone of entrance for the system fed with glucose was marginally less than that fed with starch. We surmise that the modest reduction in hydraulic conductivity was due to the rapid growth of microbial biofilm, with the growth enhanced by the greater biodegradability of the glucose.
- 2. During a subsequent four month study, COD removal rates for glucose- and starch-fed SSF CW averaged 91 and 92% respectively. These removal rates were recorded at organic loading rates equivalent to 20-22 g COD/m².d, which were three times higher than the rates used in the previous study (5-6 g COD/m².d). These results further substantiate the conclusion that SSF CWs are not sensitive to the type of organic matter with respect to removal of COD. The removal efficiency for ammonium-N was somewhat major than in the previous study and averaged 57% and 43% for the glucose- and starch-fed SSF CW.
- 3. The application of a physico-chemical pretreatment to remove suspended solids from the wastewater influent did not significantly improve effluent concentrations of COD, ammonium-N or turbidity. Removal rates for COD ranged from 76 to 86% for the system with physico-chemical pretreatment and 88 to 91% for the system with only primary sedimentation. Respective removal rates for ammonium-N ranged from 63 to 94% for the system with physico-chemical pretreatment and 65 to 91% for the system with only primary sedimentation. However, over the course of eight months, the pretreatment process removed significant amounts of suspended solids (78 mg/L with phsico-chemical-pretreatment vs 27 mg/L for primary sedimentation). Based on these findings, it is

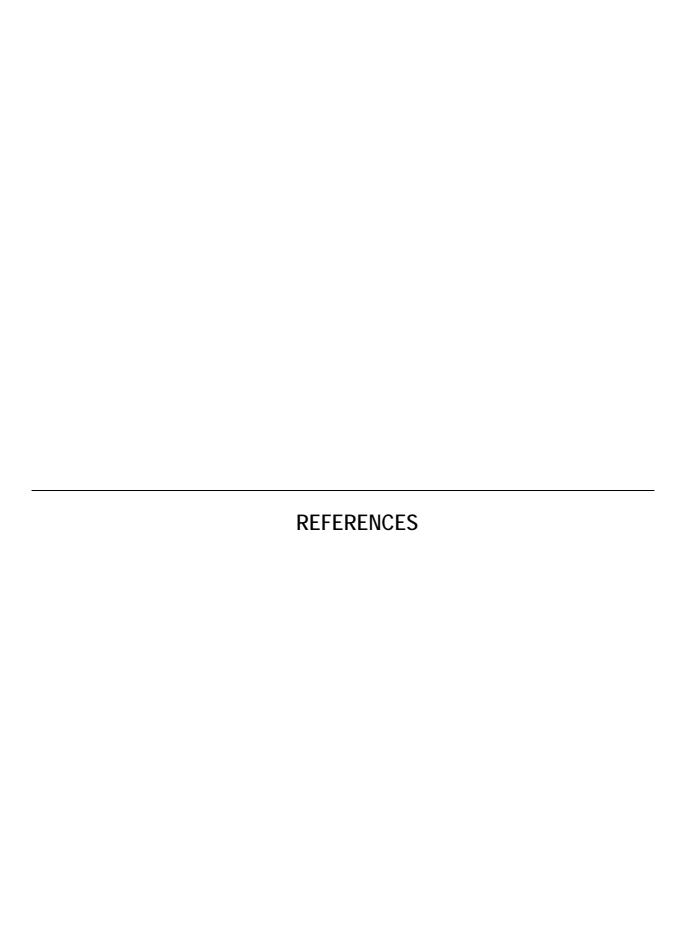
estimated that the physico-chemical pre-treatment could extend the life-span of a SSF CW by as much as ten years.

- 4. Intermittent feeding of synthetic wastewater in shallow experimental SSF CW resulted in significantly higher oxidation-reduction values and thus a more oxidized treatment environment. COD removal rates were very similar and averaged 77% and 78% respectively for the intermittently- and continuously-fed systems. However, ammonium-N removal was more sensitive to the oxidation status, and removal ranged from 80% to 99% in the intermittently fed system as compared to 71 to 85% in the continuously fed system. Furthermore, macrophyte above-ground biomass provided significant effects with respect to COD and ammonium-N removal. In experimental SSF CW systems with high above-ground biomass, COD and ammonium-N removal rates averaged 81 and 98% respectively, while systems with low above-ground biomass had average values of 73 and 72% respectively.
- 5. After several years of operation, commercial-scale SSF CW can accumulate significant quantities of recalcitrant solids in the zone of entrance. In a field survey of six full scale SSF CW, solids accumulations in the zone of entrance ranged from 3 to 57 kg/m², while solids accumulation in the outlet zone ranged from 2 to 16 kg/m². The results of this study show that there is a positive relationship between the amount of accumulated solids and the organic loading rate. The amount of organic matter in the accumulated solids was usually quite low (<20%) and was found to be very recalcitrant with respect to biological decay. Lower hydraulic conductivity values were observed near the inlet of the SSF CW (0-4 m/d), where solids accumulation was also greater. At the outlet, hydraulic conductivity values were higher (12-200 m/d).

Based on the results and analyses of these investigations, the following recommendations should be considered for further research:

- Initiate long-term multi-year studies to monitor the cumulative effects of dissolved and particulate organic matter on sediment accumulation, hydraulic conductivity and wastewater treatment efficiency.
- Continue studies to further refine and optimize the use of intermittent and batch loading to enhance nitrification and denitrification.

- Investigate new design features in the zone of entry to reduce the impact of clogging and to allow for management of accumulated solids.
- Continue studies on use of various physico-chemical pretreatments to reduce suspended solids in the influent wastewater. Also, begin evaluating up-flow anaerobic bioreactors to reduce organic loading to the SSF CW.



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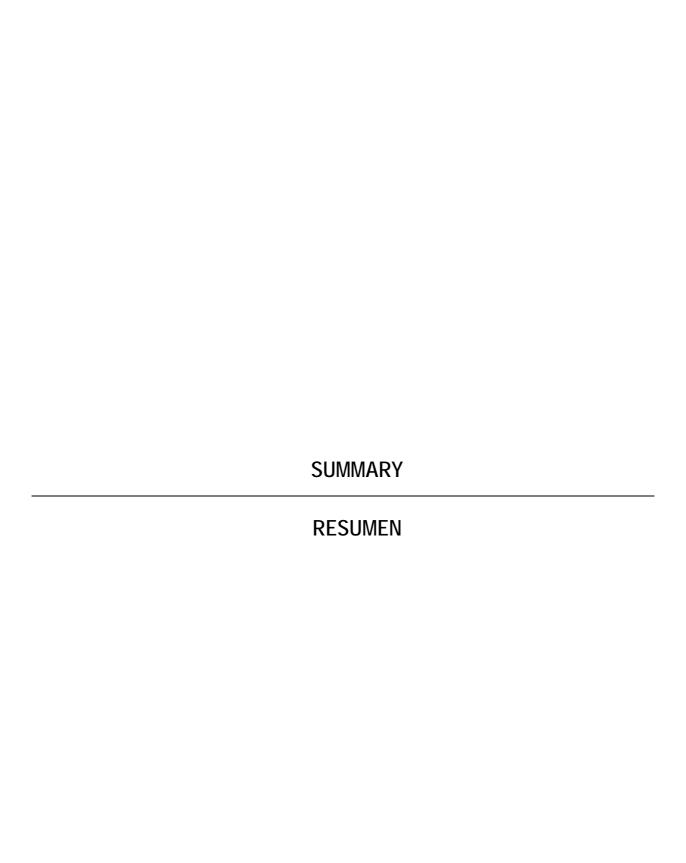
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SUMMARY

Subsurface-flow constructed wetlands (SSF CWs) constitute a proven technology for treatment of urban wastewater. One of the principal objectives of CW treatment is to remove organic matter, suspended solids and nutrients from the settled wastewater. The organic and mineral matter contained in urban wastewater is composed of a complexity of substances of different sizes and chemical compositions. In conventional treatment systems it has been demonstrated that the particle size-frequency distribution of the influent wastewater can affect treatment efficiency. However, very few studies have been conducted in SSF CW to determine whether factors such as the size-frequency distribution or organic matter characteristics affect treatment efficiency. Thus the initial hypothesis of this work is based on the supposition that in SSF CW systems, the characteristics of the dissolved and particulate organic matter can influence the removal of COD and ammonium of wastewater. The designed studies were conducted in small experimental SSF CW units that were shallow (0.27 and 0.3 m), and with a surface area of 0.54-0.77 m². The SSF CWs were planted with *Phragmites australis* and in most of the studies the treatments received wastewater on an intermittent basis. Wastewater used in these studies was either synthetic or settled urban wastewater. The synthetic wastewater was prepared with tap water and composed of glucose (organic matter easily biodegradable), starch (organic matter slowly biodegradable) and nutrients.

In Chapters 2 and 3, details are provided to illustrate that shallow SSF CW provided excellent removal of COD, with average removal rates ranging from 70 to 94% irrespective of the type of organic substrate (glucose vs starch) or organic loading rates (5-6 g COD/m².d to 20-22 g COD/m².d). The ammonium-N removal in these systems was moderate, with the glucose-fed SSF CW providing marginally better removal (45 to 57%) as compared to the starch-fed system (40 to 43%). The hydraulic conductivity was low in the system fed with glucose due to the presence of a greater growth of biofilm.

In experimental SSF CW treating urban wastewater, the application of the physico-chemical pretreatment did not improve COD effluent concentrations as compared to the no-pretreatment control (82 vs 88%), but did reduce turbidity and COD concentration in the influent. The removal rates of ammonium-N were similar in both systems and ranged from 63 to 94%. The hydraulic conductivity was higher (28 m/d) in the system with treated wastewater as compared to the control (20 m/d). These results indicate that the pretreatment could possibly help to reduce pervasive solids accummulation in the inlet zone (Chapter 4).

Chapter 5 describes a study designed to evaluate treatment efficiency in experimental SSF CW that were operated with either intermittent or continuous feeding. The COD removal rates were relatively high and merely identical in both systems, with an average value of 78%. Ammonium-N removal was significantly higher (P<0.05) in the intermittently fed system as compared to the continuously fed system (87 vs. 69%). The enhanced removal of COD and ammonium-N observed in the present studies were attributed to several factors including shallow wetland beds, macrophyte aboveground biomass, and more oxidizing conditions in the root zone.

Chapter 6 provides survey-type information for six full-scale SSF CW. The data indicated that the greatest amount of solids were deposited within the inlet zone (3-57 kg/m²), with significantly less solids near the outlet (2-16 kg/m²). It was apparent that the amount of solids deposited near the inlet was highly variable and was correlated with respective loading rates (3.1-17.5 g COD/m².d; 2.6-10 g TSS/m².d). Analyses of the accumulated solids showed them to be approximately 20% organic matter, extremely recalcitrant and difficult to degrade under either aerobic or anaerobic conditions. Hydraulic conductivity values were significantly lower near the inlet zone (0-4 m/d) as compared to the outlet zone (12-200 m/d).

Chapter 7 lists the main conclusions for each of the chapters and provides suggestions for future investigations.

RESUMEN

Los sistemas de humedales construidos de flujo subsuperficial horizontal (HCFSS) constituyen una tecnología válida para la depuración de aquas residuales urbanas. Uno de los principales objetivos de estos sistemas es eliminar la materia orgánica, los sólidos y los nutrientes presentes en el agua residual decantada. La materia orgánica y mineral contenida en el agua residual se compone de una mezcla compleja de sustancias de diferentes tamaño y composición química. En sistemas de tratamiento convencionales se ha demostrado que la distribución de tamaños de partículas del agua residual afluente puede afectar la eficiencia del tratamiento. Sin embargo, muy pocos estudios han sido llevados a cabo en HCFSS para determinar si los factores como la distribución de tamaño o características de la materia orgánica afectan la eficiencia del tratamiento. Por lo tanto, la hipótesis inicial de este trabajo está basada en la suposición de que en HCFSS, las características de la materia orgánica disuelta y particulada pueden afectar la eficiencia de eliminación de materia orgánica (DQO) y amonio. Los estudios realizados para probar esta hipótesis, fueron desarrollados utilizando pequeños contenedores experimentales poco profundos (0.27-0.3 m) con un área superficial de 0.54-0.77 m². Estos sistemas fueron plantados con *Phragmites* australis y en la mayoría de los experimentos fueron alimentados de forma intermitente. El agua residual utilizada fue de dos tipos, sintética y agua residual urbana decantada. El agua residual sintética fue preparada con agua de grifo y compuesta de glucosa (materia orgánica fácilmente biodegradable), almidón (materia orgánica lentamente biodegradable) y nutrientes.

En los capítulos 2 y 3 se hace una descripción sobre la eficiencia de los HCFSS experimentales. Estos sistemas tuvieron excelente eliminación de DQO con eficiencias entre 70 y 94% independiente del tipo de sustrato (glucosa o almidón) y de la carga orgánica superficial suministrada (5-6 g DQO/m².d y 20-22 g DQO/m².d). La eliminación de amonio en estos sistemas fue moderada, el sistema alimentado con glucosa tuvo mayor eficiencia (45-57%) con respecto al sistema alimentado con almidón (40-43%). La conductividad hidráulica fue menor en el sistema alimentado con glucosa, probablemente debido a un mayor crecimiento del biofilm.

En los HCFSS que operaron con agua residual urbana decantada, la aplicación de un pretratamiento físicoquímico no mejoró la concentración de DQO en el efluente comparado con el sistema que no recibió tratamiento físico-químico (82 vs 88%), pero redujo la turbiedad y la concentración de DQO en el afluente. La eliminación de amonio fue alta y similar en ambos sistemas con un rango entre 63 y 94%. La conductividad hidráulica fue mayor (28 m/d) en el sistema con agua residual tratada que en el sistema que no recibió tratamiento (20 m/d). Los resultados de este estudio sugieren que un pretratameinto físico-químico podría evitar la acumulación de sólidos en la zona de entrada de los HCFSS.

El capítulo 5 describe un estudio diseñado para evaluar la eficiencia de eliminación en dos sistemas experimentales que operaron en forma intermitente y continua. Las tasas de eliminación de DQO fueron altas y similares en los dos sistemas con un valor promedio de 78%. La eliminación de amonio fue significativamente mas alta (P<0.05) en el sistema alimentado en intermitente comparado con el sistema alimentado en continuo (87 vs 69%).

El capítulo 6 proporciona información sobre la cantidad y calidad de sólidos acumulados en el medio granular de 6 humedales construidos a escala comercial. Los resultados de este estudio indicaron que la mayor cantidad de sólidos fue depositada en la zona de entrada (3-57 kg/m²) con diferencia significativa para la zona de salida (2-16 kg/m²). Esta alta cantidad de sólidos acumulada en la zona de entrada fue variable y estuvo relacionada con la carga orgánica y de sólidos recibida (3.1-17.5 g DQO/m².d; 2.6-10 g SST/m².d). El contenido de materia orgánica de los sólidos acumulados fue bajo (20%) y de difícil biodegradación tanto en condiciones aeróbicas como anaeróbicas. Los valores de conductividad hidráulica en estos sistemas fueron bajos (0-4 m/d) cerca de la zona de entrada con respecto a la zona de salida (12-200 m/d).

Por último, en el capítulo 7 se enumeran las principales conclusiones de cada uno de los aspectos estudiados y se mencionan algunas sugerencias para futuras investigaciones.

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CURRICULUM VITAE

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147