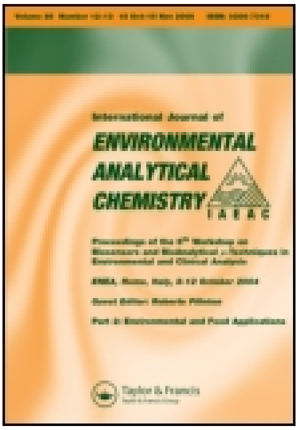

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

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Available online: 16 May 2011

To cite this article: José Villaseñor, Javier Mena, Francisco J. Fernández, Rocío Gómez & Antonio de Lucas (2011): Kinetics of domestic wastewater COD removal by subsurface flow constructed wetlands using different plant species in temperate period, International Journal of Environmental Analytical Chemistry, 91:7-8, 693-707

To link to this article: http://dx.doi.org/10.1080/03067319.2010.497918

Intern. J. Environ. Anal. Chem.
Vol. 91, Nos. 7–8, 15 June–15 July 2011, 693–707

Kinetics of domestic wastewater COD removal by subsurface flow constructed wetlands using different plant species in temperate period

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(*Received 14 December 2009; final version received 24 May 2010*)

The objective of this work has been to study the kinetics of domestic wastewater chemical oxygen demand (COD) removal when using constructed wetlands (CWs) with different plant species and at different water depths. Kinetic rate constants were obtained by using several kinetic models, and also combined with different hydraulic models. Synthetic wastewater was fed to five identical pilot-scale CWs, planted with different species (CW1: unplanted; CW2: *Phragmites australis*; CW3: *Lythrum salicaria*; CW4: *Cladium mariscus*; CW5: *Iris pseudacorus*). Wastewater was treated under continuous operation during 5 months. Water samples were taken along intermediate points at the wetland, and also at three different depths (top, medium depth and bottom). The COD experimental data were fitted to different kinetic models previously and extensively reported in the literature: the K-C and K-C* equations, and also the 'retardation' model. Also, the effect of the hydraulics characteristics was considered. Apart from the ideal plug flow assumption, two different flow models were used when integrating the mass balance equations: the plug flow with dispersion model and a detention time gamma distribution (DTGD) model. The more developed plants (CW3 and CW5) were the ones that caused an increase in COD removal rate compared with the unplanted wetland. Differences in COD removal rates were observed at different depths in the unplanted wetland, and the higher rate constant values were obtained near the wetlands top. On the contrary, the higher plants development in CW3 and CW5 eliminated the influence of water depth. The retardation model offered the best mathematical fitting to the experimental data. By using non ideal flow models, an increase in the rate constant values was always obtained, especially in the wetlands whose hydraulic behaviour was very far from the ideal plug flow. The rate constants values obtained using the DTGD model were higher (25–54%), compared to the values obtained if ideal flow was considered. These results could aid the design of CW, particularly in temperate periods.

Keywords: wastewater; constructed wetland; COD; kinetic model; hydraulic model; plants influence; depth influence

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067319.2010.497918
http://www.informaworld.com

1. Introduction

Horizontal subsurface flow constructed wetlands (HSSF CWs) are commonly used for domestic wastewater treatment. Their performance is based on a combination of physical, chemical and biological mechanisms that make them very complex systems and difficult to design. A correct HSSF CW design must consider different aspects, and one of them is the knowledge of the pollutant removal kinetics. Kinetic data of removal of COD, suspended solids (SS), total nitrogen (TN), total phosphorous (TP), etc. would be used in the mass balance equations which try to simulate the behaviour of such complex systems, and more research effort to obtain kinetic data would be welcomed by CW designers.

The present work tries to offer useful kinetic information of domestic wastewater COD removal by using HSSF CWs under different operating conditions. Two variables have been chosen in order to relate them with the kinetic data: the effect of the plant species used, and the water depth in the wetland. A review of the previous reported information in the literature recommended the election of these two important factors: water depth [1–3] and plants [4–6].

As can be inferred from the abundant reported information [7–9], it is not easy to determine the effect of the plant specie used in a HSSF CW performance. Brisson and Chazarenc [10] recently reported a review about the use of different plants, concluding that is difficult to obtain a direct relationship between the plant species and the wetland removal rate or removal efficiency, because a more rigorous analysis of plants' growth and composition would be needed, although finally, the positive effect of the plants' presence seemed to be sufficiently proved. With respect to the kinetic information and for design purposes (especially if plants growth and characterisation is not the main knowledge area of a CW designer), it would be useful to obtain removal kinetic rate constants for HSSF CWs using different plant species, and compare with kinetic constants of unplanted control wetlands.

The water depth is also an important factor because it could be directly related to the oxygen transfer from the atmosphere or the potential aeration effect of the plants roots. However, the literature reported regarding this factor is not particularly abundant. García *et al.* [11] showed the effect of HSSF CWs depth on their kinetic rate constants values, and reported that slower biochemical oxygen demand (BOD_5) removal was found at greater depths. The different removal rates at different depths could help decide the total depth during the design of a HSSF CW.

Kinetic constants can be evaluated by choosing an adequate kinetic equation, and fitting the simulated pollutant concentration profile to the experimental concentration data. Rousseau *et al.* [12] reported a review of the different kinetic models which could be used for a model-based design of a HSSF CW. The most commonly used equations are the well known K-C and K-C* first-order models, Equations (1) and (2) respectively [13], which became an important design tool despite their simplicity. An appendix is included at the end of this article to explain the nomenclature and symbols used in the work.

$$\frac{C_{\mathrm{out}}}{C_{\mathrm{in}}} = \exp(-K \cdot t) \tag{1}$$

$$\frac{C_{\mathrm{out}} - C^*}{C_{\mathrm{in}} - C^*} = \exp(-K \cdot t) \tag{2}$$

C_{in} and C_{out} ($\mathrm{mg\,L^{-1}}$) mean the inlet and outlet pollutant concentrations, while C^* ($\mathrm{mg\,L^{-1}}$) means the final or residual background concentration. Different alternative equations have been proposed in the recent years which try to improve the K-C and K-C* first-order models, including a better description of the kinetic behaviour inside the wetland. One of them is the time-dependent retardation model for COD removal reported by Shepherd *et al.* [14]. This is a first-order model that considers a decreasing average kinetic rate constant (Equation 3) because the pollutants composition is changing along the wetland, the easily biodegradable substances are removed first and fast, leaving a wastewater with less biodegradable constituents and hence with slower removal kinetics.

$$K = \frac{K_0}{b \cdot t + 1} \tag{3}$$

where K_0 (d^{-1}) means the initial ($t = 0$) first-order volumetric rate constant, and b is the time-based retardation coefficient. Kadlec [15] reported that each individual pollutant compound should be eliminated with a different rate and that there should be, hence, a K-value distribution through the different matter fractions of the total pollutants mixture. He proposed a K values gamma distribution [16], Equations (4) and (5):

$$f(x) = \frac{1}{\beta \cdot \Gamma(n)} \left(\frac{x}{\beta}\right)^{n-1} \cdot \exp\left(-\frac{x}{\beta}\right) \tag{4}$$

$$\Gamma(n) = \int_0^\infty x^{n-1} \cdot e^{-x} \cdot dx \tag{5}$$

For a K gamma distribution, $K = x$ in Equations (4) and (5), and these equations include also shape parameters (β and n). When $n = 1$, the gamma distribution becomes the exponential distribution, and the integration of a batch first-order model would become the time-dependent retardation model, with $\beta = b$ [14] which was previously presented in the literature without the supporting concept of the K value distribution function.

Variable-order or Monod-type models and mechanistic-compartmental models have also been proposed [12,17,18]. Both type of models proved to be correct and accurate options, but mechanistic models are so complex that they do not offer real help for design purposes.

An adequate and well-calibrated kinetic model has to be included in the mass balance equation which would become the HSSF CW design equation. However, a second important aspect has to be considered: the hydraulic flow model. The flow behaviour of a CW is expressed by a hydraulic model. Different hydraulic models have been widely applied to obtain a better understanding of CW flow and as design tools applicable to modelling CWs as chemical reactors. These hydraulic models and their parameters are fitted to detention-time distribution (DTD) curves, which in turn are derived from tracer experiments [13]. The batch or ideal plug-flow model has been the most usual model used for wetlands design, but more realistic models should also be considered.

The most common hydraulic models applied to the DTD curves are the Plug-Flow with Dispersion (PFD) model and the Tank-In-Series (TIS) model [18]. The latter is a special case of the Detention-Time Gamma-Distribution (DTGD) model [15], which assumes that the water molecules have a gamma distribution of hydraulic retention time values. All these models can be calibrated by obtaining the values of the different parameters: the dispersion number (D/uL) for the PFD and the 'number of tanks' (N) for the TIS and DTGD models. Equations (6) and (7) show the DTD curves of PFD and DTGD models, respectively. Both the dispersion number and its inverse, the Peclet number, mean the axial dispersion of the flow, where D is the axial dispersion coefficient ($m^2\,d^{-1}$), L is total wetland distance form inlet to outlet (m) and u is the longitudinal velocity ($m\,d^{-1}$).

$$E_{\mathrm{PFD}}(t) = \frac{e^{-\frac{\left[1-\left(\frac{t}{\bar{t}}\right)\right]^2}{4\cdot\left(\frac{D}{uL}\right)\cdot\left(\frac{t}{\bar{t}}\right)}}}{2\cdot\bar{t}\cdot\sqrt{\pi\cdot\left(\frac{D}{uL}\right)\cdot\left(\frac{t}{\bar{t}}\right)}} \tag{6}$$

$$E_{\mathrm{DTGD}}(t) = \frac{N}{\bar{t}\cdot\Gamma(N)}\left(\frac{N\cdot t}{\bar{t}}\right)^{N-1}\cdot\exp\left(-\frac{N\cdot t}{\bar{t}}\right) \tag{7}$$

where the function $\Gamma(N)$ is calculated with Equation (8).

$$\Gamma(N) = \int_0^\infty t^{N-1}\cdot e^{-t}\cdot dt \tag{8}$$

The combination of both kinds of models, kinetic and hydraulic, must be considered in order to obtain a correct design equation describing the degradation process of a pollutant along the wetland.

In this context, the aim of this work is to obtain K data for COD removal by HSSF CW treating artificial domestic wastewater, and to evaluate the effect of two factors: the plant species used and the water depth. The mathematical approach used to obtain the K values used different options of kinetic and hydraulic models, so indirectly these two factors have been also studied. This work tries to report realistic K data that would be useful for wetlands design.

2. Experimental

2.1 *The experimental installation*

The pilot-scale experimental installation used was situated on a farm near Ciudad Real, in southern Spain (Figure 1). The installation consisted of a synthetic domestic wastewater-feeding system, five HSSF CWs and a system for purified-wastewater collection. The feeding system consisted of a $1.5\,m^3$ water tank with temperature control, a 50-litre concentrated substrate tank and two peristaltic pumps to feed the 20 L mixing tank with (tap) water and the concentrated substrate; five additional peristaltic pumps continuously fed the parallel wetlands. The wetlands consist of five experimental mesocosms formed by $2.5\,m \times 0.65\,m$ channels with a bed depth of 0.6 m, situated on a covered platform in order to protect them from the rain, with a longitudinal slope of 1%. A different species of macrophyte was planted in each wetland except for wetland 1, which was used as a control without plants. Plants were bought in commercial greenhouses and were put in the wetlands during the previous summer. The distribution of species was as follows: CW1, control; CW2, *Phragmites australis* (Reed); CW3, *Lythrum salicaria* (Purple Loosestrife); CW4, *Cladium mariscus* (Sedge); and CW5, *Iris pseudacorus* (Yellow Flag). All the CWs were filled with gravel with a particulate diameter of 6–9 mm, apart from the top and bottom 10 cm layers, for which the particulate diameter was 9–12 mm to improve the distribution of wastewater in the CW. Sampling points were placed along the HSSF-CWs at ¼, ½ and ¾ of the total length. They consisted of vertical plastic tubes (5 cm diameter)

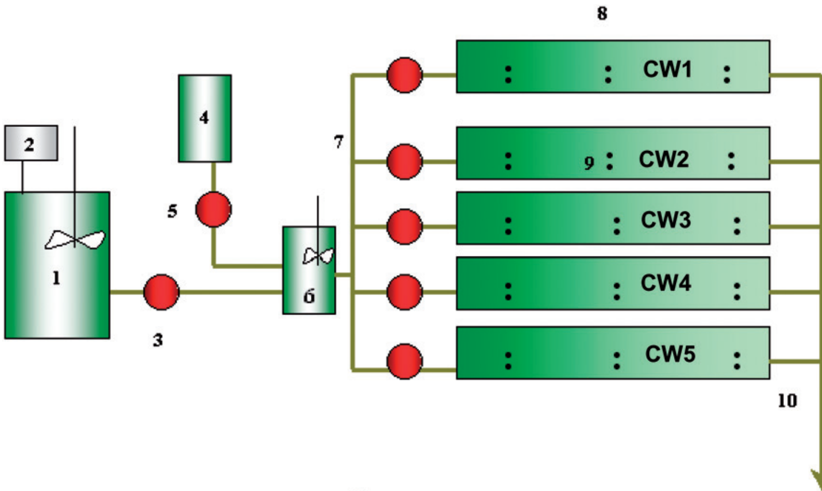

Figure 1. Diagram of the experimental installation: (1) water tank; (2) T control; (4) concentrated substrate tank; (3,5) peristaltic pumps; (6) feed mixing tank; (7) peristaltic pumps; (8) wetlands; (9) sampling points; (10) treated water outflow.

perforated with several small holes (1 cm diameter) at different positions. The tubes were put in the wetlands before filling the wetlands with gravel. They allowed to introduce temperature, dissolved oxygen or redox probes, and also to take samples at different depths. Finally, the depurated water was conducted into a collecting system.

2.2 *Procedure: operating conditions, sampling and analysis*

Synthetic wastewater was used in order to have a correct control of the wastewater characteristics. The synthetic wastewater simulated a low-loaded domestic physically pre-treated wastewater. A concentrated substrate was used and later diluted with tap water in order to prepare the synthetic wastewater. The average inlet wastewater composition was: glucose = 153 mg L^{-1}, powdered milk = 60 mg L^{-1}, Na_2CO_3 = 25 mg L^{-1}, KH_2PO_4 = 10 mg L^{-1}, $MgSO_4 \cdot 7H_2O$ = 1.5 mg L^{-1}, $FeCl_3 \cdot 6H_2O$ = 2.5 mg L^{-1}, KCl = 2 mg L^{-1} and $(NH_4)_2SO_4$ = 66 mg L^{-1}. The average inlet wastewater parameters were as follows: TSS = 117 mg L^{-1}, COD = 197 mg L^{-1}, BOD_5 = 101 mg L^{-1}, TN = 16 mg L^{-1}, N–NH_4^+ = 9 mg L^{-1}, N–NO_x^- = 1.5 mg L^{-1}, TP = 2.9 mg L^{-1} and SO_4^- = 160 mg L^{-1}.

All the wetlands were continuously fed and monitored using wastewater during 5 months (March–July), with a previous start-up period of 6 months. They were fed with a mean inlet flow of 40 l d^{-1} in order to maintain a mean theoretical hydraulic residence time ($\bar{t}$) of 9.6 days in each HSSF CW and an average inflow COD loading of 4.8 g COD m^{-2} d^{-1}. The temperature of the inflow wastewater was set at 25°C, with the temperature control system located in the tap water tank, in order to obtain an approximate constant T level in the water inside the wetlands. As a result, the temperature of the water measured inside the wetlands were always 19 ± 3°C. Water samples were weekly taken by triplicate from the inlet and outlet flow, and at three water depths for each intermediate sampling point (0.0 m, 0.3 m and 0.6 m depth, that is wetland surface, medium depth and wetland

Table 1. Values of the hydraulic parameters obtained in the tracer experiments.

Wetland	D/uL	N
HSSF CW1	0.187	2.7
HSSF CW2	0.309	1.6
HSSF CW3	0.166	3.0
HSSF CW4	0.153	3.3
HSSF CW5	0.143	3.5

bottom respectively). The way of sampling at intermediate points was as follows: a small glass tube (50 mL) was introduced slowly into an intermediate sampling plastic tube to the desired depth, and a water sample was collected after 5 minutes. All of the relevant parameters were analysed in the laboratory (COD, Total N, Total P, SO_4^{2-}, NH_4^+–N, NO_3^-–N and NO_2^-–N) according to the standard methods [20], although this work only shows COD results.

The previous hydraulic characterisation of the 5 HSSF CWs was also necessary for the calculation of K constants when using non-ideal flow models. The dispersion number (D/uL) for the PFD model, and the 'number of tanks' (N) for the DTGD model, were calculated by tracer tests as reported by Mena *et al.* [21]. The tracer tests consisted of injection of a bromide solution at the CW inlets and the measurement of the bromide concentrations over several days at the CW outlets. One litre of a sodium bromide solution (5000 mg L^{-1}) was fed as a single pulse in each CW. After the pulse, the wastewater feeding was kept continuous and effluent samples were collected at different times. The bromide concentration of each sample was measured by ion chromatography using an 'IC Metrohm' chromatograph with a 'Metrosep Anion Dual 2' anionic column and a conductivity detector with suppression. The values of the hydraulic parameters (D/uL, and N) obtained from the tracer experiments have been included in Table 1. Then, these results were also used for K calculations as indicated in the Results and discussion section.

2.3 *Mathematical approach*

The values of the K rate constants for COD removal were calculated in all continuous experiments, using the different plants and at different water depths. In order to calculate K values, the COD theoretical profile was developed by integration of the differential COD mass balance equation. Then, the COD concentration experimental profile along the wetland, obtained for each experiment, was fitted to the integrated equation. Mathematical fitting was done by using Microsoft Excel® software, using the SOLVER tool. An initial K value was assigned to the integrated equation and, after several iterations, the K value that yielded the minimum of sum of squared errors between simulated and experimental COD data was chosen as the best estimate.

Different options were used to obtain the integrated COD mass balance equation, depending on the kinetic model and the hydraulic model considered. The different kinetic models used were the following: the K-C and K-C* models, the time-dependent retardation model, and a K values gamma distribution, all of them previously described in the Introduction section. The different hydraulic models were the plug flow model (PF), the plug flow with dispersion model (PFD) and the detention time gamma distribution

Table 2. Mass balance equations used in this work, obtained by combining different kinetics and hydraulic models.

Hydraulic model→ ↓ Kinetic model	PF	PFD	DIGD
K-C	$\frac{C_{out}}{C_{in}} = \exp(-K \cdot t)$	$\frac{C_{out}}{C_{in}} = \frac{4 \cdot a \cdot \exp\left(\frac{1}{2} \cdot \frac{uL}{D}\right)}{(1+a)^2 \cdot \exp\left(\frac{a}{2} \cdot \frac{uL}{D}\right) - (1-a)^2 \cdot \exp\left(-\frac{a}{2} \cdot \frac{uL}{D}\right)}$	$\frac{C_{out}}{C_{in}} = \frac{1}{\left(1+\frac{K \cdot \bar{t}}{N}\right)^N}$
K-C*	$\frac{C_{out}-C^*}{C_{in}-C^*} = \exp(-K \cdot t)$	$\frac{C_{out}-C^*}{C_{in}-C^*} = \frac{4 \cdot a \cdot \exp\left(\frac{1}{2} \cdot \frac{uL}{D}\right)}{(1+a)^2 \cdot \exp\left(\frac{a}{2} \cdot \frac{uL}{D}\right) - (1-a)^2 \cdot \exp\left(-\frac{a}{2} \cdot \frac{uL}{D}\right)}$	$\frac{C_{out}-C^*}{C_{in}-C^*} = \frac{1}{\left(1+\frac{K \cdot \bar{t}}{N}\right)^N}$
Retardation model	$C_{out} = \frac{C_{in}}{(1+b \cdot t)^{K_0/b}}$		
K gamma distribution			$\frac{C_{out}}{C_{in}} = \int_0^\infty \frac{E(t)}{(1+b \cdot t)^{K_0/b}} \cdot dt$

$a = \sqrt{1 + 4 \cdot K \cdot \bar{t}(D/uL)}$

Table 3. Approximate data and qualitative information regarding plants growth.

	Plants	Height (*m*) at the end of the experiments	Mesocosms surface covered by plants at the end (%)	General growth observed
HSSF CW1	No plants	–	–	–
HSSF CW2	*Phragmites australis*	1,0	50	Good
HSSF CW3	*Lithrum salicaria*	1,4	60–70	Good
HSSF CW4	*Cladium mariscus*	0,3	<5	Poor
HSSF CW5	*Iris pseudacorus*	1,5	>80	Very good

model (DTGD). Table 2 shows the combination of hydraulics-kinetics used for K calculations in all experiments and the integrated COD mass balance equation obtained for each combination. The integration details for equations showed in Table 2 have been previously reported [13,15,19,22].

3. Results

As previously reported by Villaseñor *et al.* [23], the continuous processes were maintained under steady state operation. Dissolved oxygen concentrations were very low in the entire bulk liquid of all the CWs. Also redox potential values were very similar in all wetlands, dealing with facultative anaerobic environments. All planted wetlands improved pollutants removal compared with the unplanted control wetland. The performances in terms of COD, Total N, Total P and SO_4^{2-} removal obtained by the different CWs were in the ranges 80–90%, 35–55%, 15–40% and 45–60%, respectively. *Lythrum salicaria* and *Iris pseudacorus*, which have been related with their greater growth (Table 3), were always the most efficient species that improved not only nutrients plants uptake but also other microbial removal processes probably due to a higher aeration potential, such as nitrification or aerobic respiration. All these results were obtained during a temperate

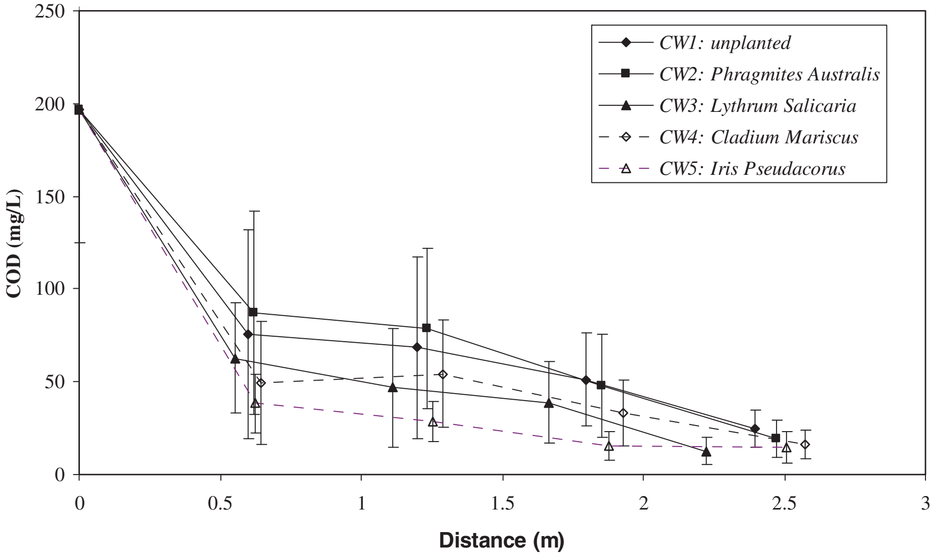

Figure 2. Average experimental COD profiles along the wetlands.

period (March–July) because it was relatively easy to control temperature. Experimental results during very hot or very cold periods were not considered because of temperature changes.

Figure 2 shows the results of COD concentration experimental data along the 5 wetlands, at the inlet, outlet and the three intermediate sampling points. Each data point is obtained as the mean of 22 weekly COD values, and the standard deviation bars are also shown. Every week COD data in the intermediate points was obtained, in turn, as the mean of the three values at the three depths: top, medium high and bottom position of the sampling points. The results indicated higher COD removal rates in all planted wetlands compared with the unplanted one, except for CW2. Table 4 shows the results of the kinetic parameters obtained from the mathematical fitting of the COD values in Figure 1 to the different mass balance equations shown in Table 1. The results indicated that, apart from the influence of the plant used, the *K* values depend also on the kinetic and hydraulic models used. The effect of these two factors will be discussed in the following section, before the discussion of the plants' influence takes place. Temperature was not considered as an additional factor, and it was assumed a constant T level during the whole work, as indicated in Section 2.2.

Figure 3 shows the results of COD concentration experimental data along CW1 and CW5, at three different depths. Each COD experimental data shown is the mean of 22 weekly measurements. The effect of water depth has been studied in all wetlands, but only CW1 and CW5 results are plotted, because they showed the higher differences between wetlands. The COD profiles shown in Figure 3a indicated a faster COD removal at the wetland top and a slower COD removal at the wetland bottom. On the contrary, Figure 3b showed nearly identical COD profiles at every wetland depths. Table 5 shows the results of the kinetic parameters obtained from the mathematical fitting of the COD values, at different depths in all wetlands, to the different mass balance equations shown in Table 1. In this case, only ideal plug flow has been considered.

Table 4. Kinetic parameters obtained from the fitting of COD data to the equations indicated in Table 2.

↓ Kinetic model		CW1 (unplanted)	CW2 (*Phragmites australis*)	CW3 (*Lithrum salicaria*)	CW4 (*Cladium mariscus*)	CW5 (*Iris pseudacorus*)
		Plug flow (PF)				
K-C	K (d^{-1})	0.25	0.22	0.37	0.35	0.55
	r^2	0.9139	0.9459	0.9451	0.9087	0.9700
K-C*	K (d^{-1})	0.51	0.31	0.63	0.76	0.83
	C^* ($mg\,L^{-1}$)	39	24	26	32	18
	r^2	0.9501	0.9412	0.9716	0.9509	0.9953
Retardation	K_0 (d^{-1})	0.75	0.38	0.96	1.98	2.26
	b (d^{-1})	1.11	0.29	1.08	3.66	3.01
	r^2	0.9704	0.9550	0.9838	0.9753	0.9986
		Plug flow dispersion (PFD)				
K-C	K (d^{-1})	0.31	0.29	0.45	0.42	0.65
	r^2	0.9407	0.9622	0.9629	0.9338	0.9800
K-C*	K (d^{-1})	0.57	0.34	0.71	0.87	1.01
	C^* ($mg\,L^{-1}$)	34	11	22	29	16
	r^2	0.9587	0.9516	0.9768	0.9639	0.9966
		DTGD				
K-C	K (d^{-1})	0.33	0.34	0.49	0.45	0.69
	r^2	0.9500	0.9658	0.9716	0.9419	0.9846
K-C*	K (d^{-1})	0.58	0.34	0.72	0.91	1.07
	C^* ($mg\,L^{-1}$)	30	0	19	27	15
	r^2	0.9612	0.9658	0.9785	0.9660	0.9971
K gamma distribution	K_0 (d^{-1})	0.23	0.22	0.41	0.68	1.32
	b (d^{-1})	0	0	0.07	0.78	1.40
	r^2	0.9864	0.9655	0.9878	0.9773	0.9987

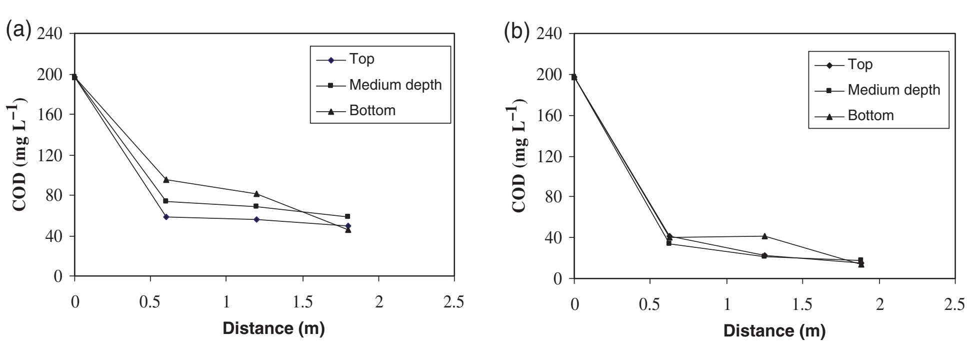

Figure 3. Experimental COD profiles along CW1 (a) and CW5 (b) at different wetland depths.

Table 5. Kinetic parameters obtained from the fitting of COD data at different depths. Only ideal PF has been considered.

Wetland depth ↓		CW1 (unplanted)	CW2 (*Phragmites australis*)	CW3 (*Lithrum salicaria*)	CW4 (*Cladium mariscus*)	CW5 (*Iris pseudacorus*)
		K-C model				
K (d^{-1})	Top	0.31	0.26	0.44	0.38	0.56
	Medium	0.25	0.21	0.33	0.33	0.62
	Bottom	0.22	0.20	0.40	0.34	0.48
		K-C* model				
K (d^{-1})	Top	0.85	0.45	0.62	0.82	0.79
	Medium	0.57	0.27	0.62	0.73	0.93
	Bottom	0.57	0.27	0.62	0.73	0.93
C^* (mg L^{-1})	Top	41	41	17	29	16
	Medium	43	17	32	33	17
	Bottom	21	20	30	32	20
		Retardation model				
K_0 (d^{-1})	Top	2.86	0.68	0.83	2.41	1.82
	Medium	0.94	0.30	1.00	1.78	3.83
	Bottom	0.32	0.29	1.01	1.82	1.82
b (d^{-1})	Top	7.25	0.82	0.58	4.50	2.07
	Medium	1.69	0.15	1.38	3.33	6.04
	Bottom	0.18	0.17	1.32	3.32	2.40

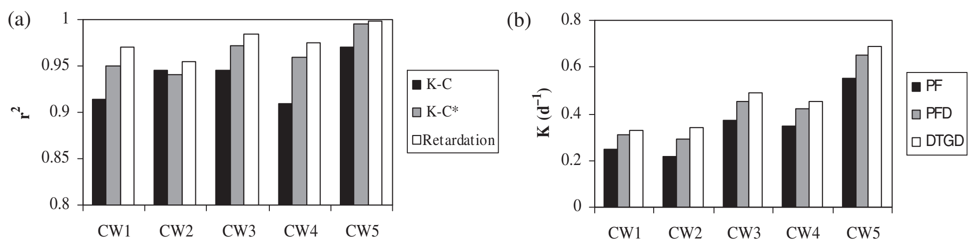

Figure 4. Fitting regression coefficients from K calculations, using the PF model and different kinetics models (a); K values obtained using the K-C model and different hydraulic models (b).

4. Discussion

Influences of kinetic and flow models have first been discussed, and subsequently the effect of plants' and wetlands' depth. The results from Section 3 have been combined in the following sections and figures in order to discuss the different variables under study.

4.1 *Effect of the kinetic and flow models*

Figure 4 shows the influence of the kinetic model (Figure 4a) or the hydraulic model (Figure 4b) used for average COD removal K calculations (Figure 2) in all wetlands.

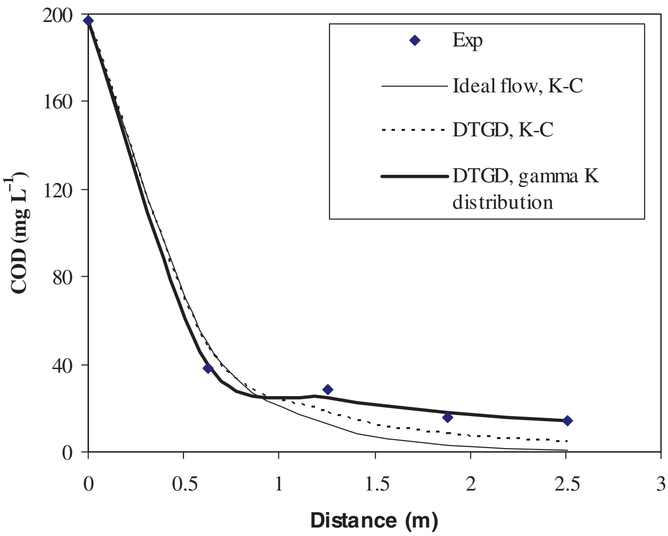

Figure 5. Simulated COD profiles in CW5 using different combinations of hydraulic and kinetic models.

Figure 4a plots the regression coefficients obtained from the mathematical fitting when using ideal plug flow and three different kinetic equations, the K-C, K-C* and the time-dependent retardation model. It can be observed the same r^2 evolution in all wetlands. The K-C model is the simplest option but obtained the lower regression coefficients, while the retardation model offered the best ones. The variable first-order *K* proposed by Shepherd *et al*. [14] allows a better mathematical fitting, and the *K* decrease (Equation 3) correctly simulates the decrease of the average biodegradability of the pollutants mixture across the wetland. Kadlec [15] clearly indicated that nothing happens to the component rate constants during passage of time; rather, it is the composition of the pollutants' mixture that changes. Anyway, the retardation model obtained good simulation accuracy. Variable-order or Monod-type models, not used in this work, would have been an interesting option, very useful to simulate biological processes.

Figure 4b shows the average COD removal *K* values obtained when using the K-C model and different hydraulic models (PF, PFD and DTGD). It can be observed the same *K* evolution in all wetlands. The lower *K* values are always obtained when ideal flow is supposed. PF model is an idealised description of flow conditions in wetlands. By using PF assumption, the *K* value obtained is an 'apparent value', lower than the real one, because it includes the negative effects of the possible flow imperfections: dead zones or preferential flow pathways. On the contrary, PFD and DTGD models are better mathematical tools, that would allow one to consider the effect of possible flow imperfections. Thus, by using non-ideal flow models, the *K* value obtained is nearest to the real value. The previous tracer studies done in all wetlands [21] showed a better fitting when using the DTGD model. The advantage of the DTGD model, compared to the usual TIS model, is that *N* is not an integer value necessarily [15]. Figure 4b shows that the *K* values obtained by using PFD or DTGD options increased approximately 25–32% in all wetlands if these values were compared to the ones calculated when using ideal PF, except CW2 which showed a *K* increase of 54% (CW2 flow was the farthest of an ideal flow). A better hydraulic design of the experimental wetlands, close to an ideal flow, would have increased the COD removal rate according to these percentage values.

Figure 5 shows the simulated COD profiles when using different kinetic and hydraulic models, and compared to the experimental data in CW5. This figure is shown as an example and similar results were obtained in all wetlands. A better simulation was obtained when gamma distributions for both K values and for residence times were used.

4.2 *Effect of the plants*

The effect of the different plants used could be discussed by comparing the K values shown at Figure 4b. The K-C model has only one representative kinetic parameter (K), so it is easy to make a comparison between the different wetlands, while for example using K-C* (with K and C^* values) or using the retardation model (with K_0 and b) would be a more difficult option if the results between wetlands must be compared. Figure 4b shows that CW3 and specially CW5, obtained higher K values. Both CW3 and CW5 were the wetlands with the higher developed plants. As reported by Brisson and Chazarenc [10] it is not easy to establish a direct relationship between the plant species and the wetlands performance, except that the presence of plants improves the efficiency of an unplanted system. Different measurements regarding plants growth and characteristics should be considered in order to find differences between the effects of different species, but in our case, only the plant size ranking could be related to the results obtained. Previous works using the same experimental system, plants and operational conditions [23,24] studied relationship between the plant species and pollutant removal efficiencies and conditions reached in the wetland (water dissolved oxygen concentrations and redox potentials), and only statistical significant differences with the unplanted wetland were obtained when using high developed plants. In this work, *Lythrum salicaria* (Purple Loosestrife) and *Iris pseudacorus* (Yellow Flag) were the plants that reached the largest size under the specific operating conditions, and obtained also the higher K values. In order to know if there were significant differences in COD removal efficiencies, a one-way ANOVA test was done using the results of the five continuous processes. The results showed that differences only could be significant if we compare CW3 and CW5 with the rest of wetlands, and only at intermediate distance in the wetlands.

Lythrum salicaria (Purple Loosestrife), *Iris pseudacorus* (Yellow Flag) and *Cladium Mariscus* (Sedge) are very common species in the natural wetlands in central Spain, especially in the 'Tablas de Daimiel' National Park, located in a dry region, which has the highest Sedge population in Europe. These three species still have not been enough considered for HSSF CW wastewater treatment studies, according to the review presented by Brisson and Chazarenz [10].

It was surprising the low K values that were obtained when using *Phragmites australis* (CW2) despite a good plant growth. The hydraulic study previously done [21] indicated that CW2 was very far from the ideal flow and flow imperfections could be probably the reason of the low K values obtained. Indeed, as indicated before, a higher (52% increase) and more realistic K value was obtained by using the DTGD flow model.

If the K-C* model or the retardation model were used to discuss the plants influence, similar conclusions could be obtained. The results in Table 4 indicate that K (from K-C*)

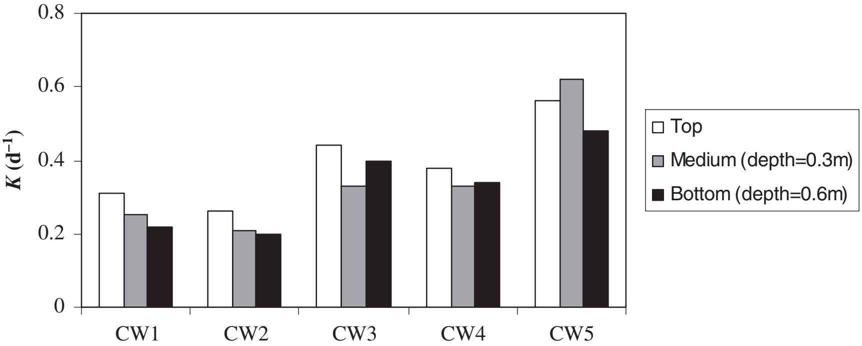

Figure 6. K values obtained using the K-C model at different water depths in the wetlands.

and K_0 are always higher in CW3 and CW5, and lower in CW1 and CW2, which corresponds with the above discussion.

The inclusion of C^* accounts for the generation of organic matter within the wetland, input from atmospheric or ground sources, and existence of a recalcitrant fraction of the COD [13]. The slowly biodegradable COD fraction (including the inert fraction) of the wastewater used was approximately 35%. It was measured using the method proposed by De Lucas *et al.* [25]. The fact that C^* values obtained in this work were always higher in the unplanted wetland and lower in CW5, would argue for the presence of a slowly biodegradable or recalcitrant COD fraction that would be better removed if well developed plants were present, rather than residual matter produced by plants. Very little information exits on suitable values of C^*. The C^* values reported in this work are similar to the ones reported by Stein *et al.* [26].

4.3 *Effect of water depth*

As indicated before, the CW1 COD profiles in Figure 3a showed faster COD removal at the wetland top and slower COD removal at the wetland bottom. A previous work discussed the mechanisms involved in the COD removal in these experiments [23] and the higher oxygen transfer rate at the wetlands top was used to justify the higher aerobic COD removal rate at this position. Also, García *et al.* [11] previously reported that greater BOD_5 removal rates (and therefore, greater COD removal rates) were found at lower depths, that is, positions near the wetland top. On the contrary, no influence of depth was found in COD removal profiles in Figure 3b (CW5), and the results were nearly identical. Figure 6 shows the K values obtained using the K-C model at different water depths in the wetlands, also shown in Table 5. There is a decreasing trend for K values in CW1, while there is not a clear trend in CW3 and CW5, the wetlands with more developed plants. It seems that plants cause a vertical homogenisation of COD removal rates, and increased the K values compared to the unplanted wetland. This effect, a improvement of COD removal efficiency at every depth, would be caused by different effects related to the presence of the roots at higher depths: higher biofilm microbial activity and oxygen access to deeper zones in the wetland, effects which have been widely reported in the literature [27,28].

Finally, a brief comparison between K values reported in this work and the ones found in the literature has been done. Values of K (mainly at 20°C) vary widely in the literature. US EPA [29] suggested that BOD_5 K_{20} ranged from 0.80 to 1.85 d^{-1} while

Rosseau *et al.* [12] reported values from 0.22 to 0.86 d^{-1}, also for BOD_5 removal. Regarding COD removal rates, Reed *et al.* [30] suggested $K_{20} = 1.1\, d^{-1}$, Kadleck and Knight [13] reported K_{20} values from 0.3 to 6.1 d^{-1}, and Stein *et al.* [26] reported values from 0.36 to 0.92 d^{-1}. The present work (Table 4) offered values from 0.22 to 0.83 d^{-1} (using ideal plug flow, and K-C or K-C* kinetics).

5. Conclusions

From the results obtained when calculating the COD removal rate constants, the following conclusions could be indicated:

Sedge and yellow flag, the more developed plants, were the ones that caused an increase in COD removal rate compared with the unplanted wetland. Differences in COD removal rates were observed at different depths in the unplanted wetland, and the higher rate constant values were obtained near the wetlands top. On the contrary, the higher plants development in CW3 and CW5 eliminated the influence of water depth. The time-dependent retardation model offered the best mathematical fitting to the experimental data. By using non-ideal flow models, an increase in the rate constant values was always obtained, especially in the wetlands whose hydraulic behaviour was very far from the ideal plug flow. The rate constants obtained using the DTGD model were higher (25–54% increase, compared to the ones if ideal flow was considered). These results would help CW design although they would be particularty useful under temperate periods.

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Appendix 1. Nomenclature

b	time-based retardation coefficient (d^{-1})
BOD_5	biochemical oxygen demand ($mg\,L^{-1}$)
$C*$	pollutant outlet background concentration ($mg\,L^{-1}$)
C_{in}	pollutant inlet concentration ($mg\,L^{-1}$)
C_{out}	pollutant outlet concentration ($mg\,L^{-1}$)
COD	chemical oxygen demand ($mg\,L^{-1}$)
CW	constructed wetland
D	dispersion coefficient ($m^2\,d^{-1}$)
D/uL	dispersion number (dimensionless)
DTD	detention-time distribution
DTGD	detention-time gamma distribution
$E(t)$	experimental detention-time distribution curve
HSSF	horizontal subsurface flow
K	kinetic rate constant (d^{-1})
K-C	first order kinetic model
K-C*	first order kinetic model with background pollutant concentration
K_0	average K value for $t=0$ in the retardation model (d^{-1})
L	total wetland distance form inlet to outlet (m)
N	number of tanks
PFD	plug flow with dispersion
SS	suspended solids
t	batch time (d)
$\bar{t}$	mean calculated hydraulic residence time (d)
T	temperature (°C)
TIS	tank-in-series
TN	total nitrogen ($mg\,L^{-1}$)
TP	total phosphorus ($mg\,L^{-1}$)
u	longitudinal water velocity ($m\,d^{-1}$)