Kinetic study and removal of contaminants in the leachate treatment using subsurface wetlands at pilot scale

Estudio cinético y remoción de contaminantes en el tratamiento de lixiviados empleando humedales subsuperficiales a nivel piloto

Estudo cinético e remoção de contaminantes no tratamento de lixiviados usando zonas húmidas subsuperfície no nível piloto

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Abstract

The treatment of stabilized leachate from the Curva de Rodas landfill site in Medellin, Colombia, was evaluated using horizontal subsurface flow constructed wetlands (HSSF) planted with *Phragmites australis* at pilot scale. Assays were performed in two stages: the first with hydraulic loads (q) of 0.015 and 0.030md^{-1} and the second with loads of 0.060 and 0.091md^{-1}. A wetland without plants was used as a control. Removals of 71.9, 91.2 and 75.1% for COD, BOD$_5$ and NH$_4^+$-N, respectively, were obtained. Kinetic constants were determined for each q or hydraulic time retention for COD, BOD$_5$ and NH$_4^+$-N with ranges into 0.103 and 0.413d^{-1}, 0.065 and 1.208d^{-1}, and 0.113 and 0.418d^{-1}; respectively, in accordance with a first order under piston flow. And by linear regressions had a magnitude of 0.246 d^{-1} for the removal of COD (R^2 = 0.955), 0.299d^{-1} for NH$_4^+$-N (R^2 = 0.922) and 0.199d^{-1} for BOD$_5$ (R^2 = 0.140). The elimination of mercury, lead, arsenic and zinc was also evaluated, achieving removals of: 37.8-92.9% Hg, 29.9-44.9%Pb, 7.9-77.6%As and 22.9-64.3%Zn, depending on the hydraulic load applied. The accumulation of these metals in the leaves, stems and roots (rhizomes) of *Phragmites australis* was found as: 0.575-3.201mgHgkg^{-1}, 0.649-4.718mgPbkg^{-1}, 3.548-39.376mgZnkg^{-1}, and 19.4mgAskg^{-1}.

Keywords: kinetic, leachate, metals, removal, wetland.

Resumen

Se realizó la evaluación del tratamiento del lixiviado estabilizado del Relleno Sanitario Curva de Rodas de la ciudad de Medellín-Colombia, empleando humedales subsuperficiales de flujo horizontal (HSSF) a nivel piloto plantados con *Phragmites australis.* Los ensayos fueron realizados en dos etapas, la primera etapa con cargas hidráulicas (q) de 0,015 y 0,030md^{-1} y en la segunda etapa con 0,060 y 0,091md^{-1}. Un humedal sin plantas como control fue usado. Se obtuvieron remociones del orden de 71,9, 91,2 y 75,1% para el COD, BOD$_5$ y NH$_4^+$-N, respectivamente. Se determinaron las constantes cinéticas para cada q o tiempo de retención hidráulica de COD, BOD$_5$ y NH$_4^+$-N; con rangos entre 0,103 y 0,413d^{-1}, 0,065 y 1,208d^{-1} y 0,113 y 0,418d^{-1}, respectivamente; según un modelo de primer orden sobre flujo a pistón. Y por regresión lineal se tuvieron magnitudes de 0,246d^{-1} para la DQO (R^2 = 0,955), 0,299d^{-1} para NH$_4^+$-N (R^2 = 0,922) y 0,199d^{-1} para DBO$_5$ (R^2 = 0,140). También se evaluaron las remociones de mercurio, plomo, arsénico y zinc alcanzándose los siguientes rangos de remoción: 37,8-92,9% Hg, 29,9-44,9%Pb, 7,9-77,6%As y 22,9-64,3%Zn dependiendo de la carga hidráulica aplicada. La acumulación de estos metales en las hojas, tallos y raíces (con rizomas) de las *Phragmites australis* estuvo en los rangos: 0,575-3.201mgHgkg^{-1}, 0,649-4,718mgPbkg^{-1}, 3,548-39,376mgZnkg^{-1}, y de 19,4mgAskg^{-1}.

Palabras clave: cinética, humedal, lixiviado, metales, remoción.

Resumo

Avaliação do tratamento de lixiviado de aterro estabilizado Curva de Rodas de Medellín, na Colômbia foi realizado utilizando wetlands de fluxo de subsuperfície horizontais (HSSF) a nível piloto plantada com Phragmites australis. Os testes foram realizados em duas etapas, a primeira etapa com as cargas hidráulicas (q) de 0,015 e 0,030md^{-1} e na segunda etapa com 0,060 e 0,091md^{-1}. A zona húmida sem plantas foi usado como um controle. Remoção da ordem de 71,9, 91,2 e 75,1% para CQO, a CBO5 e NH$_4^+$, respectivamente, foram obtidos. As constantes cinéticas de COD, CBO$_5$ and NH$_4^+$-N foram determinados com intervalos entre 0,103 e 0,413d^{-1}, 0,065 e 1,208d^{-1}, e 0,113 e 0,418d^{-1}); de acordo com um modelo de primeira ordem, sob fluxo de pistão. E, por regressão linear, tínhamos magnitudes de 0,246d^{-1} para a COD (R^2 = 0,955), 0,299d^{-1} para NH$_4^+$-N (R^2 = 0,922) e 0,199d^{-1} para CBO$_5$ (R^2 = 0,140). Hg 37.8-92,9%, 29,9-44,9% Pb, As 7,9-77,6% e 22,9-64,3% Zn, dependendo da carga hidráulica aplicada: a remoção de mercúrio, chumbo, arsênico e zinco atingir os seguintes intervalos de folga também foram avaliadas. O acúmulo desses metais nas folhas, caules e raízes (rizomas) de Phragmites australis estava nos intervalos: 0,575-3,201mgHgKg^{-1}, 0,649-4,718mgPbKg^{-1}, 3,548-39,376mgZnKg^{-1}, em 19,4mgAsKg^{-1}.

Palavras chave: c*inética, wetland, chorume, metais, remoção*.

Introduction

Leachate from landfills may contain large amounts of organic and inorganic matter, which can be soluble or insoluble in water. The untreated leachate can percolate and reach groundwater sources or mix with surface water and increase contamination [1].

In the Curva de Rodas (RSCR) landfill in Medellin, Colombia is necessary to study treatment alternatives for the leachate generated in a site that was opened since 1984 until 2003. And the constructed wetlands could be functional and implemented as in Canada, Norway, Poland, Slovenia, United Kingdon and USA [2,3].

Constructed wetlands are well-designed and appropriate pretreatment systems that have shown good results in the treatment of domestic sewage, industrial wastewater, mining drainage, agricultural water, leachate and other water with similar characteristics [1,2,3]. In wetlands, the degradation of organic matter and nutrients follows a first order kinetics model with hydraulic piston flow behavior [1,4]. Various researchers, like Kadlec and Wallace [5], have made modifications to this kinetic concept. Vymazal *et al.* [6] made more complex modifications in which linear regressions were used [7]. They employed mathematically more sophisticated methods which take into account the many factors influencing the kinetics of degradation and the transport phenomena of pollutants in wetlands. Such factors include microorganisms, plants, support means (such as gravel), environmental factors and the hydraulic nature of contaminants, among others.

Since 1980 leachate treatment using subsurface horizontal flow wetlands [8] has shown that these systems are effective at removing toxic and recalcitrant residues. At the beginning, leachate from landfills has high pollutant loads of organic and inorganic matter (including heavy metals). However, over time this concentration decreases until it stabilizes [9,10,11]. It is at this point that treatment using wetlands becomes more feasible. Colombia has built a lot of wetlands for wastewater treatment, but many of them were designed by people with little knowledge of the subject. As a result, many do not work well or have closed. About 10 years ago at various universities in Colombia, serious studies began regarding water treatment using wetlands [12,13], for domestic wastewater treatment and pesticides as chlorpyrifos. And around the world and present, the wetlands are used to treat many other types of wastewater of industrial applications in combination with other constructed hybrid systems [3].

This study have considerations of the behavior of the wetlands as wastewater treatment systems, including differents conditions of hydraulic time retention and evaluating the removal of COD, BOD$_5$ and NH$_4^+$-N; specifically in leachate, contributing with the development in areas of the environmental knowledge with useful importance in a country located in a tropical region.

The main objectives of this study were: a) to evaluate the system efficiency of removal of COD, BOD$_5$ and NH$_4^+$-N of leachate in constructed subsurface wetlands at pilot scale. b) To determine the removal first-order kinetic constants of COD, BOD$_5$ and NH$_4^+$-N at diferents conditions of time

retention and together with a linear regression. c) To evaluate the removal of heavy metals (Hg, As, Pb and Zn) and their bioaccumulation in the *Phragmites australis* plants used in the wetlands.

Materials and methods

Treatment system and experimental design
The experiment was conducted at the University Research Center (SIU) of the University of Antioquia in the city of Medellin (altitude 1466 meters). Six fiberglass tanks 1.0m long, 0.6m wide and 0.6m deep were used. The support medium used in the wetlands were gravel beds of two particle sizes: a lower bed with 2.7mm grains (D_{10}) and an upper bed with 3.4mm grains. Each bed was 0.15m thick. The leachate layers of the pilot systems were maintained at a height of 20cm and the flow was supplied using ABB flowmeters.

Experiments were carried out over 163 days in two stages (with an average air temperature of 24°C), each with its respective stabilization phase of between 20 and 22 days. During each stage, the wetlands were operated at various flow rates, and with two replicates for each case. Additionally, a wetland without *Phragmites australis* was employed as a control. Wetlands were named A, B, C and D (Table 1), and the equivalences between the retention times were specified (HRTe and HRTn, effective and nominal, respectively). The equivalence in terms of hydraulic head (q) and BA, BB, BC and BD for the case of wetlands without plants or controls were also specified. Porosity was determined by draining the wetlands without *Phragmites australis*, following the procedure used by Sanford *et al.* [14], to give a magnitude of 0.32. In each wetland, six species of *Phragmites australis* were planted evenly distributed.

Table 1. Operating conditions of wetlands.

Wetlands condition	ml min^{-1}	HRTn (d)	HRTe (d)	q (m d^{-1})
STAGE 1				
A	6.3	13.2	4.2	0.015
B	12.6	6.6	2.1	0.030
STAGE II				
C	25.2	3.3	1.1	0.060
D	37.8	2.2	0.7	0.091

Leachate
The 40 hectare Curva de Rodas landfill (Table 2) is where solid waste from the city of Medellin (Colombia), and other towns near Medellín, was deposited from 1984 to 2003. Due to the fact it was closed in 2003, the leachate used in this study is now stabilized.

Table 2. Characterization of the "Curva de Rodas" leachate.

Parameter	Units	Leachate Average ± Std. Dev
COD	mgL^{-1}	642.0 ± 194.7
BOD$_5$	mgL^{-1}	115.0 ± 30.4
pH	-	8.36 ± 0.20
Total Alkalinity	mgCaCO$_3$L^{-1}	3800.83 ± 504.78
NH$_4^+$-N	mgNL^{-1}	496.17 ± 161.87
TKN	mgNL^{-1}	534.97 ± 176.15
TS	mgL^{-1}	2951.17 ± 1272.84
DS	mgL^{-1}	2623.15 ± 749.32

Physicochemical analysis
Chemical oxygen demand (COD), biochemical oxygen demand (BOD$_5$), total solids (TS), disolved solids (DS), ammoniacal nitrogen (NH$_4^+$-NpH and total alkalinity (TA) were analyzed in the laboratory of the University of Antioquia's Diagnosis and Pollution Control Group (GDCON) in accordance with the parameters established in the Standard Methods [15] for the initial characterization (Table 2) of the Curva de Rodas Leachate. And nitrates (NO$_3^-$), nitrites (NO$_2^-$), redox potential and pH were analyzed in the experimentation time with the wetlands. The GDCON laboratory is accredited for wastewater analysis by the Institute of Hydrology, Meteorology and Environmental Studies (IDEAM) of the Colombian Ministry of Environment and Sustainable Development. The metals iron, cadmium, lead, mercury, arsenic and chromium were determined using a GBC 932 plus atomic absorption (AA) instrument with a GBC GF 3000 graphite furnace. The granulometric characterization of the support medium was

performed by the mechanical method established by ASTM-D421-50 and ASTM-D422-63.

At the end of the study samples of *Phragmites australis* plants were taken and divided into leaves, stems and roots (including rhizomes) and then dried at room temperature for 4 days. Each of the samples obtained was analyzed for Pb, Zn, As and Hg. In the analysis of Pb, Zn, and As the biomass was weighed in crucibles and dried at 100°C for 12 hours until a constant weight was achieved. It was then calcined at 450°C for 16h. After that, 2ml of 2N HNO_3 was added and acid digestion was performed in a thermostatic plate. It was then further calcined for 1h and 5ml of 2N HNO_3 and 20ml of 0.02N H_2SO_4 were added. Next it was filtered with qualitative paper, diluted to 25ml and analyzed with the GBC 932 plus instrument (with a GBC GF 3000 graphite furnace). For the analysis of Hg, the biomass was weighed and the following was added: 5ml of concentrated H_2SO_4, 2.5ml of HNO_3 (65%), 50ml of Type 1 water and excess $KMnO_4$. The organic matter was then degraded in a Winkler bottle. The biomass was put in a water bath at 60°C for 2h. Hydroxylamine hydrochloride was added until the biomass was decolorized and it was then filtered. The volume was adjusted to 100 ml with Type 1 water, and finally it was measured by the AA instrument coupled with a HG3000 GBC cold steam generator.

Kinetic models

Kinetic constants of the removal of COD, BOD_5 and NH_4^+-N were determined according to the model of Crites *et al.* [1], which describes the behavior of piston flow and first-order kinetics in the degradation of pollutants in wetlands:

$$\frac{C_0}{C_i} = e^{-K_v t} \tag{1}$$

Where:

C_o and C_i are the inlet and outlet concentrations (mgL⁻¹), respectively.

t is the hydraulic retention time (cash) (EBRT) (d).

K_v is the rate constant (Volumetric) (d⁻¹).

The kinetic constants of COD, BOD_5 and NH_4^+-N were calculated individually analyzing the inflow and outflow of each wetland periodically, for the operating conditions described in the Table 1; with the propose of measure repeatability. Along with the average of the C_i and C_o concentrations obtained throughout the monitoring and by the linear regression relationship HRTe vs. Ln (C_o/C_i).

Results and Discussion

Removal in wetlands
The best removals of COD and NH_4^+-N were obtained in the operating condition "A" (q = 0.015md⁻¹) with average removals of 71.8% and 71.9% of COD and NH_4^+-N, respectively (Table 3). The lowest concentrations of COD and NH_4^+-N in the effluent were 25.2mgL⁻¹ and 27.1mgL⁻¹, respectively, indicating a significant reduction in contamination levels and leachate toxicity. In the case of BOD_5, the highest removal was 89.4%, with a concentration of 12mgL⁻¹ in the effluent.

The magnitudes of parameters as DOB in the effluent were relatively low, according with Kadlec [3], because it achieved a secondary and tertiary treatment type, with BOD ranges into the inflow and outflow of 65 and 30mgL⁻¹, and 30 and 10mgL⁻¹, respectively; decreasing the environment risks during a probably discharge into surface water.

Table 3 shows that wetlands planted with *Phragmites australis* obtained higher percentages of COD and NH_4^+-N removal compared with the control wetlands. It should be noted that the greater the HRT the longer the interaction time between the pollutants and the microorganisms attached to the rhizomes of the plants and gravel. This allows the microorganisms to better adapt to the support medium, have a greater diversity and a have higher degree of oxygenation. Therefore, the conditions offered by wetland plants lead to a greater removal efficiency of COD and NH_4^+-N. In contrast, the control wetlands (BA and BB) had higher removals of BOD_5 (91.2% each) than wetlands A and B. This could be due to higher hydraulics time retention where had more contact of facultative microbes that living in association with the substrate and plant roots, because to the microbial control exists when the nutrients loading to the wetland exceeds the hability of the vegetation to utilize it [2], influencing of this way the carbon and nitrogen removal reactions.

Table 3. Percentage of removal of COD, BOD_5 y $N-NH_4^+$ in each wetland monitored.

Wetland	Average Removal (%)		
	COD	BOD_5	NH_4^+-N
A	71.8	71.2	71.9
B	53.3	89.4	55.3
C	33.4	28.8	33.6
D	29.6	50.8	21.2
BA	53.5	91.2	53.1
BB	50.1	91.2	39.9
BC	17.8	23.2	20.3
BD	15.0	40.0	14.3

The levels of redox potential within the wetlands oscillated from 248mV to 193mV, suggesting that oxidative conditions were the mechanisms of greatest influence on the removal of COD and NH_4^+-N. In the case of NH_4^+-N, this is confirmed by the NO_2^- value of 42.866mgL^{-1} and the NO_3^- value of 133.455mgL^{-1} obtained in the effluent. The pH decreased from about 8.8 in the affluent to 7.8 in the effluent, which indicates alkalinity consumption by nitrification processes.

Kinetic constants
Table 4 shows the values of Kv for the removal of COD, BOD_5 and NH_4^+-N, which ranged from 0.115 to 0.401d^{-1}, 0.099-1.121d^{-1} and 0.114-0.402d^{-1}, respectively. These ranges are extensive because they were obtained with wetlands under different operating conditions.

Table 4. Kinetic constants for the removal of COD, BOD_5 and NH_4^+-N determined with equation.

Wetland	COD (d^{-1})			BOD_5 (d^{-1})			NH_4^+-N (d^{-1})		
	K_V	$K_{V\ Prom}$	σ	K_V	$K_{V\ Prom}$	σ	K_V	$K_{V\ Prom}$	σ
A1	0.287	0.282	0.008	0.313	0.290	0.032	0.310	0.290	0.028
A2	0.276			0.268			0.270		
B1	0.390	0.401	0.017	1.035	1.121	0.122	0.418	0.402	0.022
B2	0.413			1.208			0.387		
C1	0.128	0.115	0.018	0.065	0.099	0.049	0.115	0.114	0.001
C2	0.103			0.134			0.113		
D1	0.257	0.222	0.049	0.421	0.458	0.064	0.151	0.147	0.005
D2	0.187			0.330			0.143		

The kinetic constants for the removal of COD, BOD_5 and NH_4^+-N (Table 4) had a higher magnitude in wetland B (0.401d^{-1}, 1.121d^{-1} and 0.402d^{-1}, respectively) than wetland A (0.282d^{-1}, 0.290d^{-1} and 0.290d^{-1}, respectively). However, wetland B had a HRTn of 6.6d, which was lower than the HRTn for wetland A (13.2d), but higher than wetlands C and D (3.3d 2.2d, respectively). According to the above, a high value of Kv does not require long retention times with leachates. However, it probably does need a large microbial population in the gravel and roots of the plants to degrade the pollutants. And possibly the microbial population would had best conditions for growing at HRTn of 6.6d for wetland B accelerating the kinetic of nitrogen (as NH_4^+-N) and organic matter; and later until 13,2d the microorganisms went into a renovation and adaptation stage for the degradation of the more resistant and recalcitrant compounds of the leachate at higher time [11].

Standard deviations (σ) (Table 4) of the Kv measurements indicate that there was good repeatability in the kinetics COD and NH_4^+-N removal. Repeatability was less significant for BOD_5 removal, possibly due to the range of variation of the test in the laboratory. The kinetic constants determined with linear regressions (Table 5) had a magnitude of 0.246 d^{-1} for the removal of COD ($R^2 = 0.955$), 0.299d^{-1} for NH_4^+-N ($R^2 = 0.922$) and 0.199d^{-1} for BOD_5 ($R^2 = 0.140$), with 1.5 < q (cm d^{-1}) < 9.1. The results were more similar with the constants determined individually for the A wetlands, but a lower correlation with BOD_5 was obtained.

Table 5. Kinetic constants for the removal of COD, BOD_5 and NH_4^+-N determined for lineal regression.

Humedal	Ln(Ci/Co)	TRHe (d)	Parámetro	Ecuación	R^2	K_v (d^{-1})
A	1.19	4.2				
B	0.81	2.0	COD	Ln (C_i/C_O) = 0.246 HRTe + 0.193	0.955	0.246
C	0.40	1.1				
D	0.34	0.7				
A	1.23	4.2				
B	2.26	2.0	BOD_5	Ln (C_i/C_O) = 0.199 HRTe + 0.737	0.140	0.199
C	0.35	1.1				
D	0.71	0.7				
A	1.23	4.2				
B	0.81	2.0	NH_4^+-N	Ln (C_i/C_O) = 0.299 HRTe + 0.023	0.922	0.299
C	0.22	1.1				
D	0.23	0.7				

Rousseau *et al.* [7] obtained a series of kinetic removal constants under different conditions with a BOD_5 variation range of 0.17d^{-1} to 6.11d^{-1}. The BOD_5 constant obtained in this study by linear regression (0.199d^{-1}) and the Kv determined individually (0.099d^{-1}-1.121d^{-1}) are within the range established by Rousseau *et al.* [7]. Jing and Lin [16] gave a summary of nitrogen removal constants obtained by different authors using subsurface wetlands, showing values between 0.411 d^{-1}-0.126 d^{-1}. The values of NH_4^+-N kinetic removal constants from individual analyzes (Table 4) and linear regression (Table 5) found in this study are within the ranges reported in other research. In the A wetlands, kinetic constants were derived that were very similar to those established by linear regression for COD (0.282d^{-1} and 0.246d^{-1}, respectively) and NH_4^+-N (0.290d^{-1} and 0.299d^{-1}, respectively), bearing in mind that under these conditions the highest removal efficiencies were obtained.

In terms of leachate treatment, Metcalf and Eddy [11] suggested that for the degradation of toxic and recalcitrant compounds, it is necessary for the microorganisms to be acclimated and conditioned to this type of substance for an appropriate time. In this study such measures were carried out using wetlands where the loads to be treated were controlled, as seen in Tao *et al.* [17]. The effective operation of wetlands depends on the hydraulic and organic load, as well as the physiochemical (pH, redox potential) and biological (size of microbial population) conditions, since these factors favour the transformation of contaminants.

Removal of heavy metals in wetlands

The monitoring of metals in the leachate showed that the concentrations of chromium and copper were very low, less than 0.083mgL^{-1} and 0.042mgL^{-1} in the influent and 0.050mgL^{-1} and 0.025mgL^{-1} in the effluent, respectively. For lead, a maximum concentration in the influent of 0.313mgL^{-1} and a minimum in the effluent of 0.108mgL^{-1} was found, yielding an overall average of 29.9% removal. In the case of mercury, removals were obtained from 37.8% to 96.2% in the first stage, and 54.5% to 92.9%, in the second, for influent concentrations of 5.92mgL^{-1} to 56.12mgL^{-1}, and 9.00gL^{-1} to 16.00mgL^{-1}, respectively. In the case of zinc, in the first stage, the maximum concentration in the effluent was 0.073mgL^{-1}, with a maximum removal of 64.3%. In contrast, for the second stage, removal reached 22.9% with an affluent concentration of 0.054mgL^{-1}. The observed decline is due to an increased HRT, which resulted in a shorter time for this metal to be assimilated by plants. The removals obtained in this study are consistent with the results reported by Kröpfelová *et al.* [18] who used constructed wetlands for wastewater treatment and obtained removals between 25.7% - 84.2% for lead, 58.3% - 90.5% for zinc and 29.4% - 47.4% for mercury.

The maximum arsenic removal in the first stage was 77.6%, while in the second stage it was 70.4%. The removal of metals in wetlands may be because of plant uptake, adsorption onto the gravel and plants, and precipitation. All of these processes are favored by increasing the HRTn to times longer than 6.6 days.

Heavy metal accumulation in plants

The zinc content in the *Phragmites australis* was 39.38mgkg^{-1} in the leaves, 3.55mgkg^{-1} in the stem, and 13.72mgkg^{-1} in the roots and rhizomes. This means that a total of 69.5% of zinc was retained in the leaves (Figure 1). Lead accumulation was 4.72mgkg^{-1} in the leaves, 0.65mgkg^{-1} in the stem, and 1.07mgkg^{-1} in the roots and rhizomes. Therefore, again the highest concentrations were in the leaves, within the composition of the plant, giving an accumulation percentage of 73.3% (Figure 2). Values can be compared for the treatment of wastewater reported by Vymazal *et al.* [6,19], with levels of 0.22mgkg^{-1} in leaves and 0.13mgkg^{-1} in stems, and data taken by Vymazal *et al.* [19] where concentrations were between 0.09 and 0.21mgkg^{-1} in the leaves and stems, 2.5 to 8.0mgkg^{-1} in the roots, and 0.7 to 12.2mgkg^{-1} in rhizomes. It can be seen that lead concentrations detected in this study were consistent with data reported in the literature, as both show that the highest lead content is in the leaves.

Mercury concentrations in this study were 1.21mgkg^{-1} in the leaves, 0.58mgkg^{-1} in the stem, and 3.20mgkg^{-1} in the roots and rhizomes (Figure 3). Therefore, the highest content of Hg (24.2%) was absorbed in the root zone. This indicates that mercury is less mobile than Zn and Pb, and thus, stays in the roots and rhizomes. In terms of the accumulation percentages of heavy metals present in the plants, the leaves had highest lead and zinc content (73.3 and 69.5%, respectively), while the stem had lower percentages of lead, zinc and mercury (10.1, 6.3 and 11.5%, respectively). According to the above, the Pb and Zn were most concentrated in the leaves and roots of the plants, and less so in the stems. In contrast, the concentrations of mercury were highest in the roots, then in the leaves and finally in the stems. These results were similar to those obtained by Vymazal *et al.* [6,19]. In conclusion, in this study it was found that the concentrations of metals in the biomass of *Phragmites australis* were highest for Lead and Zinc, and lowest for mercury.
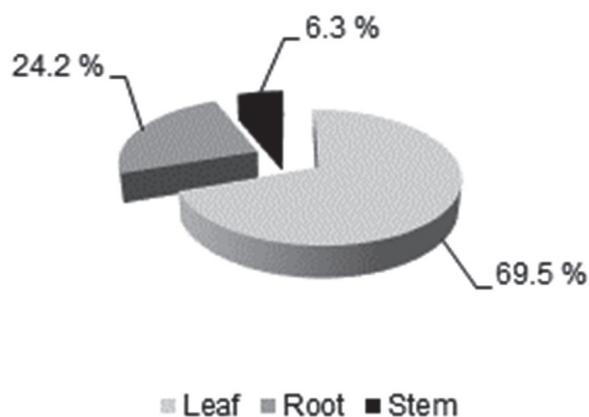

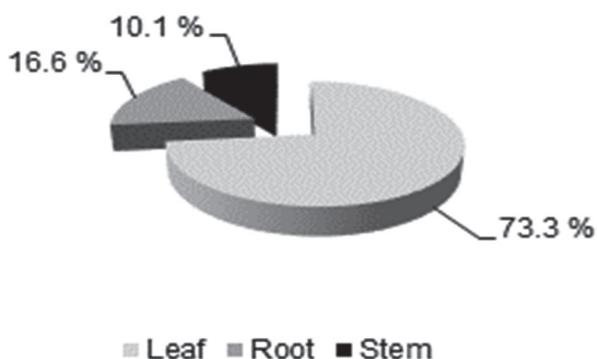**Figure 1.** Percentage of zinc accumulated in plants.

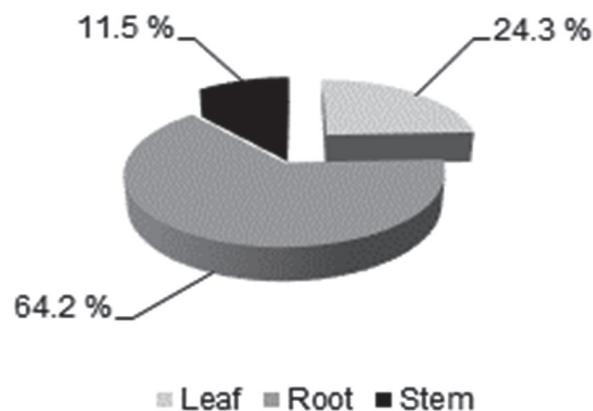**Figure 2.** Percentage of lead accumulated in plants.

Figure 3. Percentage of mercury accumulated in plants.

Kadlec and Zmarthie [8] studied too the storage and accumulation of trace metals in wetland plants in contact with leachate from a close landfill, where have been shown to accumulate metals in above and below ground tissues, but those amounts are minor in comparison to the sequestered in sedimentation. But an alternative to dispose the plants could be incineration.

Conclusion

High removal percentages of COD and NH_4^+-N of 71.9 and 75.1%, respectively, were achieved. Heavy metals were also efficiently removed from the water (37.8-92.9% of Hg, 29.9-44.9% of Pb, 7.9-77.6% and 22.9-64.3% of Zn and As, respectively), which then accumulated in the leaves, stems and roots (rhizomes) of the *Phragmites Australis* (0.575-3.201mgHgkg^{-1}, 0.649-4.718mgPbkg^{-1}, 3.548-3.9376mgZnkg^{-1}, and 19.4mgAskg^{-1} only in the stem). For the treatment of leachate in tropical conditions, the kinetic constants of COD, BOD$_5$ and NH_4^+-N removal, determined individually, were 0.103-0.413, 0.065-1.208 and 0.113-0.418d^{-1}, respectively. Those obtained from linear regressions were 0.246, 0.199 and 0.299d^{-1}, respectively, according to the basic first order model and piston flow.

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