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Study on the Heavy Metals Removal Efficiencies of Constructed Wetlands with Different Substrates

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Abstract

In this study constructed wetlands (CWs) were used to remove three heavy metals (Zn, Cu and Pb). The two tested substrates were made of coke and gravel, respectively. First order dynamic model was appropriate to describe removing of Zn and Cu. The experimental results showed that first dynamic removal rate constants of Zn in CWs with coke and gravel were 0.2326 h^{-1} and 0.1222 h^{-1}, respectively. And those of Cu in CWs with coke and gravel were 0.2017 h^{-1} and 0.3739 h^{-1}. However, removal efficiencies of Pb in the coke system and the gravel system were within 95−99%, so the first order dynamic model failed to fit the experimental data because the hydraulic resident times of Pb did not affect outlet concentration of Pb. From the removal rate constants, it is found that the coke and gravel system have different absorption efficiencies of heavy metal pollutants. Therefore, it is suggested that the removal efficiencies of heavy metals are influenced by the choice of substrates to some extent.

Keywords: Subsurface Flow Constructed Wetlands, First Order Dynamic Model, Heavy Metal Pollutant, Substrate, Removal Efficiency

1. Introduction

Constructed wetlands have the characteristics of excellent performance, minimal investment and operating cost, remarkable economical and social benefits in treating wastewater. In the past 30 years, Europe and North America had set up several thousand constructed wetlands, but the designs and the operations of CWs are mostly based on statistical data and the empirical formula. However, the removal mechanism of pollutants [1] is important bases of the engineering designs of the CWs, and can provide reliability of CWs in engineering design and operation.

There are a number of physical, chemical and (micro) biological processes in purification, like sedimentation, filtration, adsorption, microbial decomposition and chemical transformation [2]. Adsorption may play an important role in the removal process. Consequently, it is important to select those substrates of high ecological activity and adsorption capacity. There has been some recent work that has attempted to investigate the influence of different substrates [3,4]. But those researches mainly focus on the treatment of wastewater containing P and N. There remains a lack of information on heavy metals purification effects in the CWs systems with different substrates.

The aim of this present study was to investigate the removing dynamics of three heavy metal pollutant in CWs with two substrates. Since the coke and gravel differs in their porosity, their purification efficiency may be different. In the present study two CWs (coke and gravel) were set up. The effluent was collected and analyzed for heavy metal concentrations.

With the development of the China industry, heavy metal pollution became more and more serious. Base on the investigation of Yangtze River, the best quality river of the seven rivers in China, heavy metals especially Zn, Pb, Cu and Cr had polluted the water systems [5]. Considering amount of waste water containing Zn, Pb and Cu mainly discharged by steel plants and copper metallurgy plants, the water pollution on Pb, Zn and Cu were studied in this paper.

Plant plays an important role in CWs. Plant root zone and substrate absorb ionic heavy metal. We aimed to provide more data about the purification effects of CWs with different substrates. In the present study, the different heavy metals contents absorbed by plant were determined after CWs run a long time, and then the role of plant in CWs were analyzed. Finally, it is hoped that the question of stability in root zone and substrate absorption will be resolved.

The first order dynamic model, which was used to predict the removal efficiencies of the pollutants treated by CWs, should be used in the design of the CWs [2,6–8]. Though the parameter and the calculation of the equation are simple, first order dynamic model has some limitations. However it is still an appropriate equation for describing the removal mechanism of the CWs treating pollutants. In the present study, the first order model with two parameters was used to describe the removal mechanism of the different CWs.

If steady and plug flow conditions are assumed, first order dynamic model can be used to describe the reduction of pollutants. The equation can be written as:

$$\frac{dC}{dt} = -k_v \times C \tag{1}$$

$$\frac{dC}{dx} = -\frac{k}{q} \times C \tag{2}$$

where C is the concentration of the quantity concerned (mg/L), t is the hydraulic resident time (h), k_v is volumetric rate constant (h^{-1}), x is the fraction of the distance through the wetland, k is the areal rate constant (m/h), and q is the hydraulic loading rate (m/h).

The rate constant always has two expression ways-k_v and k. Literature is available on k_v with subsurface flow constructed wetland and k with surface flow constructed wetland [9]. Removal rate constant represents the removal ability of the CWs. In theory, the removal rate constant relates to temperature, medium (the amount and types of microorganisms) and pollutants. Therefore, in this study the temperature was kept between 25℃−30℃ and the removal efficiencies of three type heavy metal pollutants (Zn, Cu and Pb) were analyzed. For the microbial membranes on the substrates were pitchy and dense, we believed the microbial membranes were steady and the microorganism were adapted to system environment. In order to compare the removal ability of different subsurface flow constructed wetlands, we established this study to determine the volumetric rate constant, k_v.

Even though there are non-degradable material in CWs, atmospheric and groundwater chemical additions, chemical speciation, and the biogeochemical cycle may generate background concentrations. Kadlec and Knight proposed a two-parameter model to describe the reduction of pollutants [2]. The equation can be written as:

$$\frac{dC}{dt} = -k_v (C - C^*) \tag{3}$$

where C^* is the background concentration.

The key to a quantitative model of wetland operation is the determination of the volumetric rate constant, k_v. Solution of the equation then gives a linear relationship in the concentration logarithm with the residence time. The expression for the concentration logarithm at any residence time can be written as:

$$\ln \frac{C_o - C^*}{C_i - C^*} = -k_v t \tag{4}$$

where C_o is the outlet concentration (mg/L), C_i is the inlet concentration (mg/L).

The determination of the background concentration C^* is the process related to each factor of the wetland and the interrelationship among them. Therefore, there is not a precise definition and a calculation method for the background concentration C^*.

Based on the above discussion, we conclude that the main source of the background concentration is the heavy metals ionic on the non-degradable materials, which is mainly the heavy metals ionic existed by physic absorption form on the substrate. In our previous research, the experiments on the wetlands at different operation periods showed that the heavy metals accounted for 0.69%-1.98% (coke system) and 1.07%-3.24% (gravel system) of the heavy metal intercepted by the wetlands, respectively. With the operation time of the wetlands increasing, the heavy metals stripped from the wetland would increase. In other words, the background concentration isn't constant, but changes little with the operation time increasing. If the total amount of the heavy metal intercepted by the wetland can be calculated, the expression for the background concentration can be written:

$$C^* = 0.69\% \sim 1.98\%(\text{wt})\ (\text{for Coke system}) \tag{5}$$

$$C^* = 1.07\% \sim 3.24\%(\text{wt})\ (\text{for Gravel system}) \tag{6}$$

2. Materials and Methods

2.1. Process Description

The wetlands, located in Tongji University of Shanghai, were constructed in 2007. Two wetlands, shown in Figure 1, are filled with two different substrates (coke and gravel) with a packed bed size of 1930 mm×400 mm× 600 mm (L×W×H). PVC rectangular sink with volume of 0.6 m^3 was used for storing cistern. Structural slope is 1% of height of wetland.

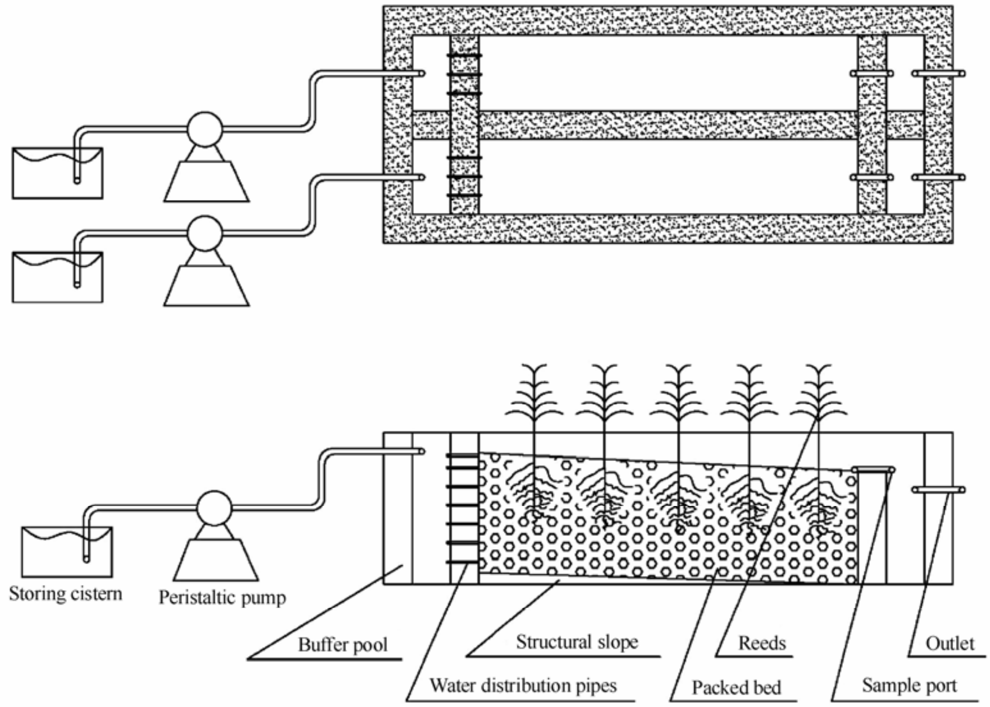

Figure 1. Flow chart of the subsurface flow constructed wetlands.

In order to compare with the treating effect of different substrates, coke with particle diameter of 5-10 mm and gravel with particle diameter of 3-8 mm were packed in the different CWs, respectively. The porosity of coke wetland and gravel wetland were 0.43 and 0.36.

Activated sludge was obtained from secondary sedimentation basin in Shanghai Quyang sewage treatment plant. Because reeds have a much better absorption of heavy metals than other species of plants [10,11], the reeds with height of 1.7 m and density of 60 plant/m^2 are used in the experiment.

Wastewater flowed into constructed wetland by Lange peristaltic pump with a model of BT00-300M, speed of 0-300 r/min and a transport regulation range of 0.07-1140 ml/min. In order to make the inflow well distributed and close to the ideal flow patterns, the water distribution pipes, shown in Figure 2, are alternately permutated. The heavy metal wastewater was lifted into the buffer tank by peristaltic pump, and then flowed into the constructed wetlands through the water distribution pipes. After being treated by the CWs, the heavy metal wastewater flowed out of the system through the sampling pipe and outlet pipe.

After the constructed wetland run for a long time, we collected reeds from inlet, medial position and outlet of constructed wetlands. First, the reeds were cleaned, and cut into seven parts. Secondly, the samples were put into crucible, dried at 70℃ at baking oven for constant weight, and weighted in turn. Thirdly, the samples were incinerated about 40min, put into muffle furnace to heat for 2 h at 600℃, treated in the processes of nitric acid hydrolysis, extraction and dilution. Finally, the samples were detected, and the heavy metals contents in reeds were determined by atomic absorption spectrometry [12].

2.2. Experiment Reagents

Heavy mental wastewater for experiment was got by Adding heavy metal salts in the water. Copper sulfate, lead nitrate and zinc sulfate are used as heavy metal pollutants. The experiment reagents and their specifications are listed in Table 1.

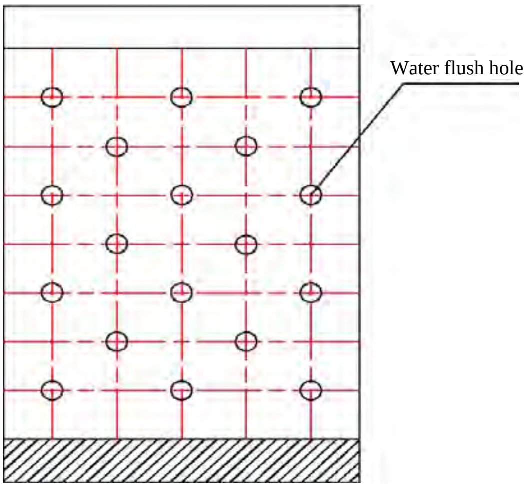

Figure 2. Drawing of water distribution system.

Table 1. Experiment reagents and their specifications.

reagents	specifications	reagents	specifications
sucrose	eatable	magnesium sulfate	analytically pure
anhydrous sodium carbonate	analytically pure	potassium dihydrogen phosphate	analytically pure
ammonium chloride	chemically pure	potassium chloride	analytically pure
copper sulfate	analytically pure	lead nitrate	chemically pure
zinc sulfate	analytically pure	lead nitrate	analytically pure
zinc oxide	reference reagent	hydrochloric acid	analytically pure

The reference standards for experiment reagents and their specifications are on the GB7475-87 standards for the reagents.

2.3. Experiment Methods and Instruments

The experiment determination standards were concentration of Cu, Zn, Pb, pH, and water temperature. The preparation of the heavy metals analyses for Cu, Zn and Pb was carried out according to China national standards GB7475-87 designed for heavy metals. The concentration of the heavy metals were detected by atomic absorption spectrophotometer (Agilent). The analyzing methods and instruments for determining water temperature according to State Environmental Protection Administration [13] approved methodology were water and exhausted water monitoring analysis method, and mercurial thermometer. According to China national standards GB6920-86, acidimeter was used to measure pH.

3. Results

3.1. Removal Efficiencies of Pb

Based on results over 4 months (September-December 2007) the removal efficiencies of wetlands treating wastewater containing Pb were calculated. The results are listed in Table 2 and Table 3. It is clearly shown in Table 2 and Table 3 that both coke and gravel systems have remarkable removal efficiencies on treating wastewater containing Pb. It was found that the removal efficiencies of the coke system and the gravel system were within 95-99%. The data of those two systems treating Pb had well agreement with the zero order dynamic model rather than the first order dynamic model. It is suggested that the Pb removal efficiencies were mainly determined by the Pb concentrations, but with little relation to hydraulic resident times.

3.2. Removal Efficiencies of Zn

The data for the events of September-December 2007 are listed in Table 4 and Table 5. According to the Equation (5) and Equation (6), the concentrations of Zn were calculated. The results are shown in Figure 3 and Figure 4. It is evident from the figures that the data follow the linear shape predicted by Equation (4). The k_v values, for the coke system and gravel system treating wastewater containing Zn were calculated and the results were 0.2326 h^{-1} and 0.1222 h^{-1}, respectively.

Table 2. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Pb at the different hydraulic loadings.

Hydraulic resident time (h)	12.68	10.72	7.99	5.73	4.76
Inlet concentration (mg/L)	27.44	23.46	19.48	21.87	11.53
Outlet concentration (mg/L)	0.0928	0.0795	0.2651	0.2883	0.5726
Removal efficiency (%)	99.66	99.66	98.64	98.68	95.03

Table 3. Inlet concentrations, outlet concentrations and removal efficiencies of the gravel system treating the wastewater containing Pb at the different hydraulic loadings.

Hydraulic resident time (h)	9.60	7.02	5.77	4.76	6.0
Inlet concentration (mg/L)	49.890	40.370	47.009	47.957	43.152
Outlet concentration (mg/L)	0.234	0.394	0.390	0.596	0.587
Removal efficiency (%)	99.53	99.02	99.17	98.76	98.64

Table 4. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Zn at the different hydraulic loadings.

Hydraulic resident time (h)	12.68	10.72	5.73	4.76	4.67
Inlet concentration (mg/L)	48.50	21.264	26.37	17.859	31.477
Outlet concentration (mg/L)	4.276	2.218	6.583	5.553	4.712
Removal efficiency (%)	91.18	89.57	75.03	68.91	85.03

Table 5. Inlet concentrations, outlet concentrations and removal efficiencies of the gravel system treating the wastewater containing Zn at the different hydraulic loadings.

Hydraulic resident time (h)	9.60	7.02	6.0	5.77	4.76	3.20
Inlet concentration (mg/L)	5.268	7.439	5.622	4.603	5.445	7.218
Outlet concentration (mg/L)	2.024	2.526	2.543	2.478	1.401	2.558
Removal efficiency (%)	61.57	66.04	54.77	46.17	74.26	64.55

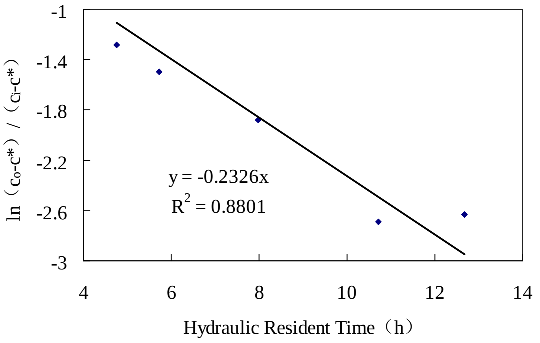

Figure 3. First-order model fitting drawing of the coke system treating Zn.

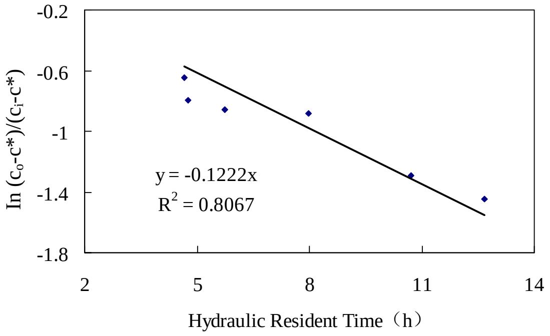

Figure 4. First-order model fitting drawing of the gravel system treating Zn.

3.3. Removal Efficiencies of Cu

The data for the event of September-December 2007 are listed in Table 6 and Table 7. According to the Equation (5) and Equation (6), the concentrations of Cu were calculated. The results are shown in Figure 5 and Figure 6.

It is evident from the figures that the data follow the linear shape predicted by Equation (4). The k_v values, for the coke system and gravel system treating wastewater containing Cu were calculated and the results were 0.2017 h^{-1} and 0.3739 h^{-1}, with coefficient of correlation R^2 0.8801 and 0.8067, respectively.

Table 6. Inlet concentrations, outlet concentrations and removal efficiencies of the coke system treating the wastewater containing Cu at the different hydraulic loadings.

Hydraulic resident time (h)	12.68	10.72	5.73	4.76	4.67
Inlet concentration (mg/L)	28.519	26.189	23.666	18.036	19.783
Outlet concentration (mg/L)	2.639	3.198	5.413	5.269	6.345
Removal efficiency (%)	90.75	87.79	77.10	70.79	67.93

Table 7. Inlet concentrations, outlet concentrations and removal efficiencies of the gravel system treating the wastewater containing Cu at the different hydraulic loadings.

Hydraulic resident time (h)	9.60	7.02	5.77	4.76	3.34	3.20
Inlet concentration (mg/L)	26.515	27.412	26.515	24.006	26.515	28.327
Outlet concentration (mg/L)	0.0735	2.268	2.577	0.0372	1.830	4.982
Removal efficiency (%)	99.72	91.73	90.28	99.84	93.10	82.40

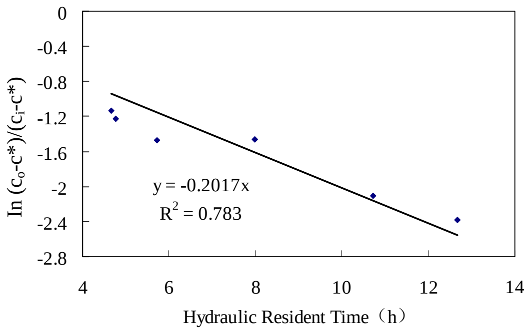

Figure 5. First-order model fitting drawing of the coke system treating Cu.

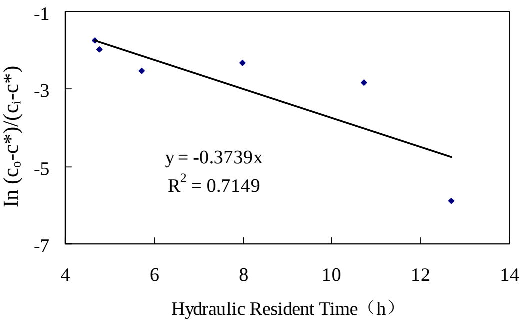

Figure 6. First-order model fitting drawing of the gravel system treating Cu.

Both the coke CWs and gravel CWs had good treatment effect on Pb. The results showed that the treatment efficiencies for Pb didn't fit for first order dynamic model. The removal efficiencies of Pb didn't change with the increasing of hydraulic retention time. The volumetric rate constants (k_v) for the heavy metals (Zn and Cu) under consideration were determined by fitting lines to the observation (Table 8).

3.4. Heavy Metals Contents in Reeds

The heavy metals contents of reeds are given in Figure 7. From the analysis of the three heavy metals, it is found that Cu, Zn and Pb contents in reeds of coke system were 0.1667%, 0.2094% and 0.2781%, respectively, and Cu, Zn and Pb contents in reeds of gravel system were 0.1645%, 0.1713% and 0.1477%, respectively. The results showed that the heavy metals contents in reed were very few. It is indicted that the reeds didn't have obvious effect on the process of CWs treating heavy metal.

Table 8. First-order model parameters of different substrates treating different heavy metal.

first order dynamic model	substrate	Heavy metal	R^2	k_V (h^{-1})
$\ln\frac{c_o - c^*}{c_i - c^*} = -k_V \times t$	coke	Zn	0.8801	0.2326
		Cu	0.7830	0.2017
	gravel	Zn	0.8067	0.1222
		Cu	0.7149	0.3739

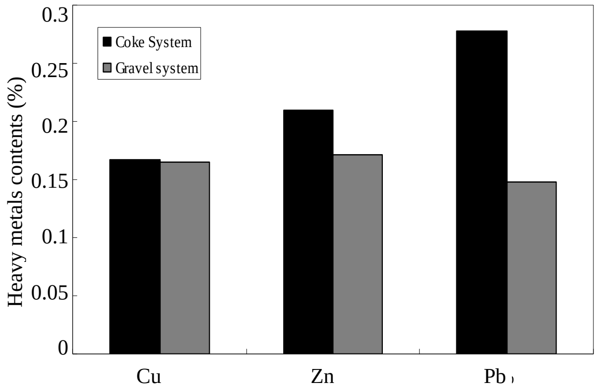

Figure 7. Heavy metals contents in reeds of different CWs based on analysis over all samples.

4. Discussion

The removal efficiencies for Pb are higher than the efficiencies for Zn and Cu. These results well agree with the discovery of Walker and Hurl [14]. The same constructed wetland has different rate constants because of the different heavy metals. The results showed that the coke system treating the Zn and Cu didn't have significant differences in the volumetric rate constant. But the volumetric rate constants of the gravel system treating Cu were higher than those of Zn. The Cu and Zn contents of reeds in gravel system didn't have significant differences. It is indicated that the CWs with gravel had better purification effect on Cu than that on Zn.

In the present study, the effects of the two different substrate systems were also investigated. Xu and Zhou found that different substrates had influence in constructed wetland treating heavy metals [3]. The results agree well with the finding of Xu and Zhou. The k_v value of the coke system treating Zn is higher than that of the gravel system. The k_v value of the coke system treating Cu is lower than that of the gravel system.

The results indicated that the first order dynamic model had its limitations, for the reason that it can't accurately describe all the heavy metal behaviors in the constructed wetland.

5. Conclusions

The study has been carried out in two constructed wetlands of different substrates (coke and gravel). The study was aimed to determine volumetric rate constants of two different substrates constructed wetlands and compared the removal ability of the different substrates. The volumetric rate constants of the coke system treating Zn and

Cu were calculated as 0.2326h^{-1} and 0.2017h^{-1}. The volumetric rate constants of the gravel system treating Zn and Cu were calculated as 0.1222h^{-1} and 0.3739h^{-1}. The volumetric rate constants of the different substrates system treating heavy metal varied. The different substrate may affect the removal ability of the constructed wetland.

This study showed that the first order dynamic model did not fit for all the heavy metals retention. The first order dynamic model could predict the Zn and Cu concentration. However, this model fail to predict Pb concentration. Both the Pb removal efficiencies of the coke system and the gravel system were within 95-99% suggesting that Pb retention had little relation to hydraulic resident times. In addiction, the Zn and Cu removal efficiencies of the coke system and the gravel system were within 54-91%, and 69-99% suggesting that the removal efficiencies for Pb are higher than the efficiencies for Zn and Cu.

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