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Kinetics of Pollutants Removal in Wetlands Influenced by Retention Time and Number of Plants Using *Cyperus alternifolius*

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ABSTRACT

Constructed wetland is considered an alternative for domestic wastewater treatment in cities. This study serves to evaluate the removal capacity and kinetics of TSS, COD, phosphate, and surfactant in domestic wastewater with several plants of *Cyperus alternifolius*, through the use of the constructed wetlands treatment. The overall objective of the study was to determine the ability of *Cyperus alternifolius* to remove water pollutants in domestic wastewater in several plants. The domestic wastewater was contacted in a batch system. The results indicated that CWs had a good performance on COD, phosphate, and surfactant with removal efficiencies of more than 80%, with a retention time of 8 days and 5 plants. However, the removal of suspended solids was found limited, as shown that the TSS removal efficiency was under 40%. The first-order equation of kinetics described the degradation of pollutants. The $q_{1/2}$ values, which were defined as the average removal loading prior to the half of the pollutant concentration being removed and represented the removal capacity without limitation of pollutants concentration, were moderately increased with an addition to the number of plants.

Keywords: constructed wetlands, *Cyperus alternifolius*, kinetics, wastewater treatment.

INTRODUCTION

Wastewater constitutes the matters that have always been the main discourse in environmental management studies. Due to the population increase caused by urban development, the water quality has also been degraded. One of the many sources of menaces for the environment is domestic wastewater, which is derived from household activities (Kulshreshtha et al., 2022). Untreated domestic wastewater causes environmental deterioration issues in rivers, lakes and different public water bodies. It has significantly developed during the last decade (Gunes et al., 2021). According to the results of a study by Indonesian Ministry of Environment Regulation No. 68 of 2016, many of the rivers in Indonesia have been polluted by untreated domestic wastewater (de Rozari et al., 2021). Vestiges of human activities in domestic wastewater include TSS, TDS, grease, COD, BOD, phosphate, nitrogen, surfactants, and organic material (Dash, 2013; Wijaya and Soedjono, 2018).

The efforts to reduce the domestic wastewater effect were made by establishing the domestic wastewater treatment. Reduction of contaminants in domestic wastewater treatment methods that may be executed consist of sedimentation, filtration, chemical precipitation, adsorption and biological treatments (Choudhary, Kumar and Sharma, 2011). One of the biological treatments that could be applied to the domestic wastewater is constructed wetlands (CWs). Several benefits of CWs include low-investment costs, absorption of carbon dioxide, minimum energy requirements, and minimum requirements for maintenance personnel (Stefanakis, 2015). These elements suggest that CWs may be carried out in densely populated regions in addition to developing regions. Apart from biological processing, the treatment processes in CWs also include filtration, sedimentation, precipitation, and adsorption. These processes enhance the reduction of the domestic wastewater contaminants entering the CWs. The potential and optimization of CWs for wastewater treatment could be influenced by several factors, including plant species, light intensity, hydraulic retention time, site-specific design, pH, temperature, media characteristics, loading rate, and dissolved oxygen (Ghosh and Gopal, 2010; Choudhary, Kumar and Sharma, 2011; Meng et al., 2014).

Kinetic studies are found to be very useful to further understand about pollutant removal processes and improve the design criteria of the existing CWs (Lyu et al., 2018). Several approaches are available to describe pollutant removal. These include first-order models and linear regression that have become the most popular models utilized in CWs to predict pollutant removal affected by pollutant concentration (Sun and Saeed, 2009; Saeed and Sun, 2011; Carvalho, Arias and Brix, 2017). Thus, on these CWs, the plant utilized for domestic wastewater treatment was *Cyperus alternifolius* which has the potential to grow rapidly in wet condition, in which it was constructed and run in batch experiment with the purpose: 1) to estimate the performance of CWs in the treatment of domestic wastewater with COD, TSS, phosphate, and surfactant parameters; 2) to examine the impact of number of plants on the performance of CWs; and 3) to analyze the removal kinetics of pollutants in CWs with different number of plants and retention time.

MATERIALS AND METHODS

The experiment was carried out at campus of Universitas Airlangga, Surabaya, Indonesia. The domestic wastewater was collected from the collection pool of wastewater installation at Genteng, Candirejo, Surabaya City, Indonesia. Some characters of the wastewater include COD: 368 mg/L, TSS: 180 mg/L, phosphate: 14 mg/L, and surfactant: 11 mg/L. The utilized batch experiment reactors were 12 L pots with the length, width, and height as follows: 20 cm, 20 cm, and 30 cm. The composition of media in the reactor consisted of 5 cm gravel (ϕ 10–20 mm) layer and 20 cm soil (ϕ 0.5–2 mm) layer. The structure of CWs is shown in Figure 1. This research utilized 16 reactors with 16 variations along with 2 replications. The implementation of domestic wastewater treatment was conducted in one stage experiment. The number of plants used was 0, 1, 3, and 5 while hydraulic retention time (HRT) was arranged as 2, 4, 6, and 8 days. The technical treatment of the domestic wastewater is elaborated in Table 1.

The domestic wastewater was provided into the reactors with a batch system of 3 L, as the effective volume for each reactor. Sampling was carried out according to a predetermined contact time then, the collected samples were analyzed for the parameter values of TSS, COD, phosphate, and surfactant. The analysis results obtained were performed with the ANOVA Two Way test to discover the optimum time in domestic wastewater treatment by CWs. The water quality analysis was conducted for the TSS, COD, phosphate, and surfactant parameters. Each parameter were altered to be similar for the analysis of subsequent procedures (Eaton et al., 2005):

- Gravimetric analysis – to determine the TSS value, dried at 103–105° C (2540 D),
- Titrimetric analysis with closed reflux – to determine the COD value (5220 C),
- Stannous Chloride analysis – to determine the phosphate value (4500-P D),
- Anionic surfactant as MBAS – to determine the LAS value (5540 C).

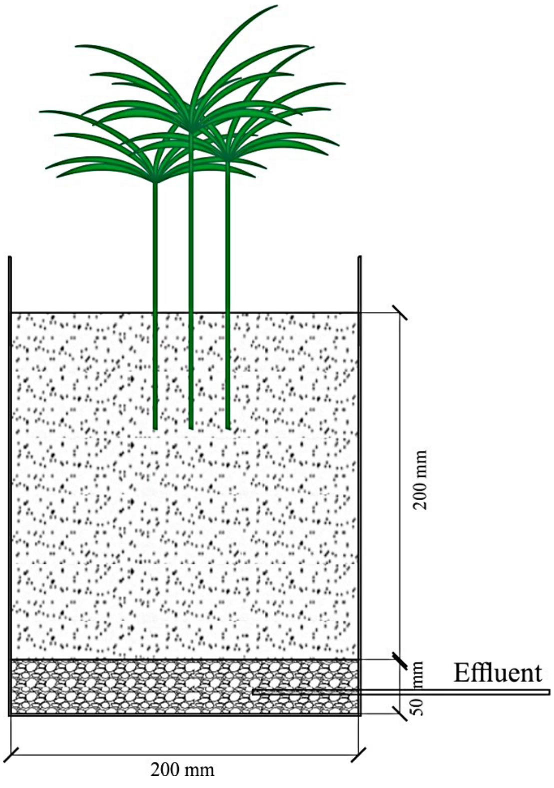

Figure 1. Schematic of reactor

Table 1. Technical treatment of domestic wastewater

Treatments		Number of Plants			
		0 plant (n_0)	1 plant (n_1)	3 plants (n_3)	5 plants (n_5)
Retention time	2 days (td_2)	$td_2 n_0$	$td_2 n_1$	$td_2 n_3$	$td_2 n_5$
	4 days (td_4)	$td_4 n_0$	$td_4 n_1$	$td_4 n_3$	$td_4 n_5$
	6 days (td_6)	$td_6 n_0$	$td_6 n_1$	$td_6 n_3$	$td_6 n_5$
	8 days (td_8)	$td_8 n_0$	$td_8 n_1$	$td_8 n_3$	$td_8 n_5$

The calculation of the pollutant removal efficiency was conducted by comparing the initial concentration value (C_d) and the final concentration (C_o) corresponding to the Equation (1) (Marzec et al., 2018):

$$RE\% = \left(1 - \frac{C_{IN} - C_{EF}}{C_{IN}}\right) \text{ x } 100\% \quad (1)$$

where: $RE\%$ – the removal efficiency of pollutants (%), C_{IN} and C_{EF} (mg/L) – the pollutants concentrations in influent and effluent, respectively.

To estimate the removal performance, the rates of pollutant decay were calculated. It was assumed that the rate coefficients could be described by using the first-order decay laws, containing the pollutant concentration (C in mg/L), the decomposition constant coefficients (k in d^{-1}), and the hydraulic retention time (t in days), which could be described as Equation (2):

$$\frac{C_{EF}}{C_{IN}} = \exp.(-kt) \quad (2)$$

For a better understanding of detailed influences of number of plants, $t_{1/2}$ and $q_{1/2}$ were introduced, which are displayed in Equation 3. Specifically, $t_{1/2}$ is the half-life of the pollutant, and is defined as the time in which the half of the pollutant was eliminated, which could be directly obtained through the degradation curve; in turn, $q_{1/2}$ is the average removal load over this period and it represents the removal capacity without any limitation on the pollutant concentration (Li et al., 2020).

$$q_{1/2} = \frac{C_{IN} V_e}{2000 t_{1/2} A} \quad (3)$$

where: $q_{1/2}$ – pollutant removal loading (g/ ($m^2 \cdot$d)), $t_{1/2}$ – the half-life of the pollutants (d), Ve – the effective volume (L), A is the surface area of CWs (m^2).

RESULTS AND DISCUSSION

Performance of CWs

The removal efficiency of pollutants in CWs is shown in Figure 2. The performance of CWs indicated a considerable removal capacity for pollutants, which was affected by the contact time. Chemical oxygen demand (COD) in wastewater signified the amount of oxygen required to oxidize organic matters. The organic material in this research was organic material from domestic

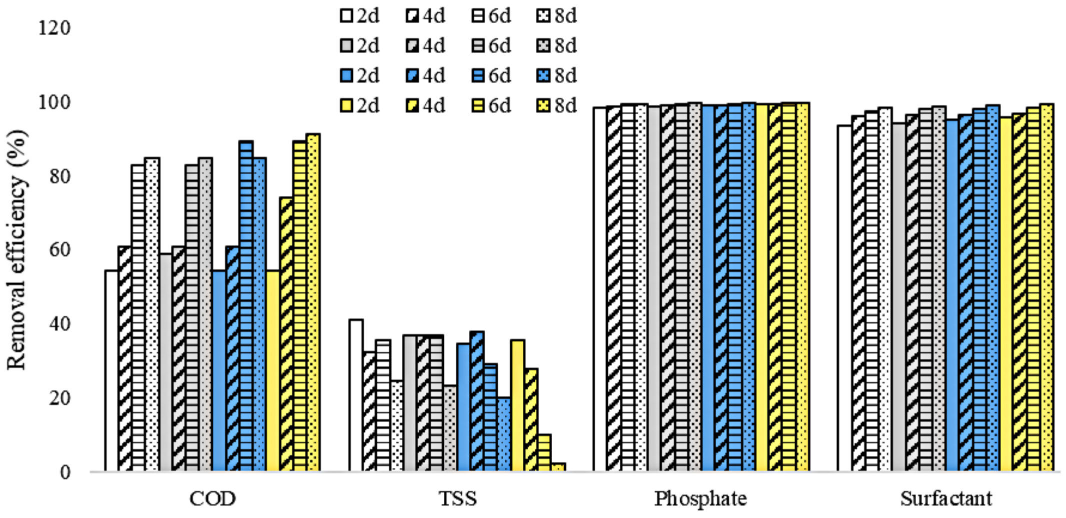

Figure 2. Removal efficiency of pollutant

wastewater. The COD concentration in domestic wastewater could reach 213 mg/L (Va et al., 2018). The COD analysis in this research utilized the closed reflux titrimetric method.

The COD removal efficiency was between 54.35 ± 3.07% and 91.3 ± 0%. Furthermore, the COD concentration in effluent was between 168 ± 11.31 mg/L and 32 ± 0 mg/L. The highest COD removal shown by the reactor had 5 plants and 8 days (td_8n_5) with the removal efficiency of 91.3 ± 0 %. Next, the lowest COD removal shown by the reactor had no plants and 2 days (td_2n_0) with the removal efficiency of 54.35 ± 3.07%. These results signified that the performance of CWs in removing pollutants was affected by the number of plants and retention time.

The research conducted by Puchlik (2016) confirmed that with CWs unit, it was possible to reduce the COD parameter of up to 79.3% by using common reed (*Phragmites australis*). The result of domestic wastewater treatment utilizing CWs with *Cyperus alternifolius* had a better efficiency of removal value than the preceding comparable studies. The COD removal in CWs emerged due to the soil, sand, and gravel media which caused filtration mechanism to eliminate organic matters. Additionally, the media could produce a bio-film which could increase the elimination of organic matters. In the research conducted by (Corbella et al., 2019) showed that the analysis of COD removal only reached 56%.

The effective removal mechanism for suspended solids (TSS) in CWs is gravitational sedimentation of discrete particles and flocculants. Gravitational sedimentation has an pivotal role in trapping the particles that are larger than 5 μm (Vymazal and Kröpfelová, 2008). Generally, the most intensive removal of suspended solids occurs in the inflow zone as a result of which these sections are usually blocked first before the water reaches the bottom of reactors. The TSS analysis in this research utilized the gravimetric method.

The results indicated that the TSS removal efficiency was between 41.11 ± 7.86% and 2.22 ± 15.71%. Furthermore, the TSS concentration in effluent was between 106 ± 14.14 mg/L and 176 ± 28.28 mg/L. The highest TSS removal shown by the reactor had no plants and 2 days (td_2n_0) with the removal efficiency of 41.11 ± 7.86%. Next, the lowest TSS removal shown by the reactor had 5 plants and 8 days (td_8n_5) with the removal efficiency of 2.22 ± 15.71%. There was no significant difference in removal efficiency of TSS in which it was affected by the number of plants and retention time. These results did not correlate with the prior research, where the TSS removal utilizing CWs to treat domestic wastewater was up to 99% (Al-Ajalin et al., 2020). This could be due to the fact that the buffer layer (gravel) utilized was not thick enough, thus increasing the likelihood that soil media particles would descend into the buffer layer and be picked up during sampling.

The phosphate in waters is presented in the form of dissolved inorganic compounds and organic compounds. Phosphate can enter water bodies through the wastewater of the population using detergents, for example in washing activities. The high phosphate content in waters can trigger the growth of plants and algae (eutrophication). The phosphate analysis in this research used the lead chloride (SnCl) method.

On the basis of the data obtained, the results of phosphate removal efficiency were between 98.32 ± 0.60% and 99.65 ± 0.05%. Furthermore, the phosphate concentration in effluent was between 0.24 ± 0.08 mg/L and 0.05 ± 0.01 mg/L. The highest phosphate removal was shown by a reactor having 3 plants and 8 days (td_8n_3). The research by García-Ávila (2020) has shown that with CWs unit, they were able to reduce the phosphate parameter up to 50% by using *Cyperus papyrus*. Meanwhile, Wahyudianto et al. (2019) reported the efficiency of phosphate removal up to 99.43% with *Equisetum hymale*. The result of domestic wastewater treatment using CWs in this research had a higher efficiency of removal compared to the previous comparable studies. Surfactants are the main component in detergents other than phosphates, and surfactants in water bodies are very difficult to degrade so that it becomes an issue if disposed of immediately without processing (Scott and Jones, 2000). The surfactant analysis in this research used the MBAS method. The results of removal efficiency for the surfactant parameter using *Cyperus alternifolius* with the number of plants and retention time variations in CWs are presented in Figure 3.

On the basis of the data obtained, the results of surfactant removal efficiency were between 93.58 ± 2.91% and 0.08 ± 0%. In turn the phosphate concentration in effluent was between 0.24 ± 0.08 mg/L and 0.05 ± 0.01 mg/L. The highest surfactant removal was shown by a reactor having 5 plants and 8 days (td_8n_5). The surfactant removal occurred due to the activity of microbial overhaul that occurred in 3 stages, namely oxidation of alkyl groups, desulfonation, and breakdown of benzene rings. The microbes in the reactor can grow on the media and roots of *Cyperus alternifolius* plants. The treatment in this research has higher capability of surfactant removal efficiency than as exhibited in (Lakho et al., 2020) research with the result obtained, which was up to 91.7%.

Kinetics study

As mentioned in the materials and methods, the samples collected from the site may reveal the pollutant removal process. All data with 4 HRT are summarized and shown together with the removal kinetic curves based on the first-order equation in Figure 3. It is clear that the curve fits the experimental data even though its value is lower for TSS after 8 days, indicating reasonableness in the selection of first-order kinetics. This is confirmed by the high coefficient of determination (listed in Table 2). Except for TSS, the coefficient of determination for other pollutants is higher than 0.6. In consideration of the variation in the initial concentration of the pollutants, the coincidence between the curves and the experimental data is acceptable for pollutants, excluding TSS.

The concentration of COD, phosphate and surfactant in the effluent is lower than the domestic wastewater quality standard, indicating that constructed wetlands can be used as an alternative technology for domestic wastewater treatment. The application of different number of plants had different removal efficiencies where the more plants used, the better half-lives and removal of loading of pollutants, except for TSS. This indicated that the number of plants provided

Table 2. Accuracies of the first-order model, half-lives and removal loading of pollutants

Parameter	n	R^2	$t_{1/2}$ (day)	$q_{1/2}$
COD	n_0	0.9459	2.40	5.74
	n_1	0.9256	2.30	5.99
	n_3	0.8504	2.25	6.13
	n_4	0.9762	1.98	6.98
TSS	n_0	0.1329	5.9	1.15
	n_1	0.1752	6.12	1.1
	n_3	0.0934	6.69	1
	n_4	0.0553	8.63	0.78
Phosphate	n_0	0.6709	0.61	0.86
	n_1	0.7139	0.58	0.91
	n_3	0.6608	0.56	0.95
	n_4	0.6218	0.54	0.98
Surfactant	n_0	0.7819	0.85	0.49
	n_1	0.8052	0.81	0.51
	n_3	0.8220	0.78	0.53
	n_4	0.8226	0.74	0.55

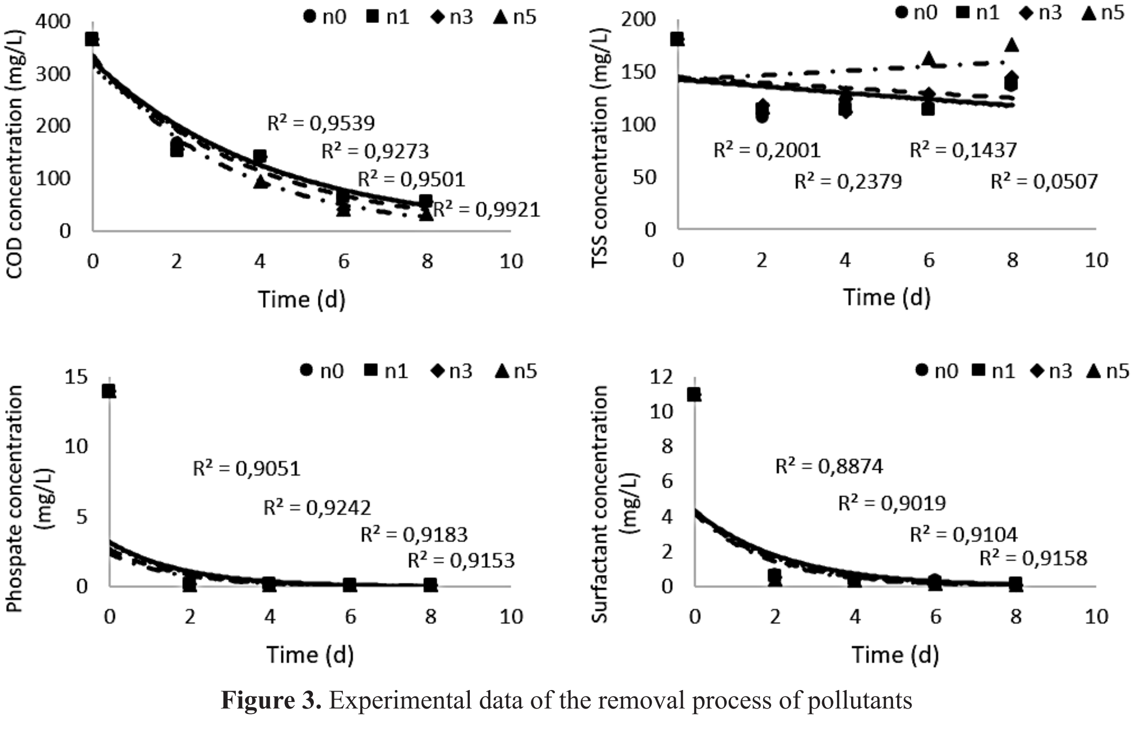

Figure 3. Experimental data of the removal process of pollutants

a source of oxygen which affects the degradation of pollutants by microorganisms in the reactors. This treatment increases the efficiency of removing organic materials such as COD, phosphate and surfactant. There was little difference between the efficiency of phosphate and removal of surfactant. Meanwhile, the COD concentration was clearly different with the increasing number of plants. However, the TSS concentration did not decrease with the number of plants. Furthermore, the maximum removal capacity of COD, phosphate and surfactant, expressed as the value of $q_{1/2}$, increasing gradually with the number of plants, indicating that the removal capacity of CWs was improved with microbial activity. Meanwhile, the $q_{1/2}$ value of TSS has shown a decrease with an increasing number of plants, caused by the possibility of clogging as mentioned earlier.

In this study, the value of $q_{1/2}$ has increased moderately, implying that the performance of CWs could be improved with the number of plants. The reactors arrangement needs to be improved especially for the thickness of the soil and buffer layer. This model can be improved in performance with more complex models and treatments, such as the replenishment of aeration (Li et al., 2020). Furthermore, in contrast to complex models, models with fewer parameters are easier to construct, and the data is easier to collect.

CONCLUSIONS

CWs show exceptional removal efficiencies for pollutants exceeding 80%, with the exception of TSS. The concentration of COD, phosphate, and surfactant has met the minimum standard of pollutants for domestic wastewater with 5 plants for 8 days. *Cyperus alternifolius* is suitable for use in CWs for domestic wastewater treatment. The number of plants can increase the removal capacity of CWs on pollutants. It could increase the $q_{1/2}$ values for COD, phosphate and surfactant moderately. However, it did not show any effect on the removal of suspended solids (TSS). Moreover, the first order kinetics can describe the removal of pollutants in the CWs reactors under a different number of plants conditions.

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