

# REDUCING AMMONIA AND CHROMIUM CONCENTRATION IN BATIK WASTEWATER BY VETIVER (*CHRYSOPOGON ZIZANIOIDES* L.) GROWN IN FLOATING WETLAND

EFFENDI, H.<sup>1\*</sup> – MARGARETHA, J. A.<sup>2</sup> – KRISANTI, M.<sup>3</sup>

<sup>1</sup>*Center for Environmental Research, Bogor Agricultural University, Indonesia*

<sup>2</sup>*Program of Natural Resources and Environmental Management, Bogor Agricultural University, Indonesia*

<sup>3</sup>*Department of Aquatic Resources Management, Bogor Agricultural University, Indonesia*

*\*Corresponding author  
e-mail: hefni\_effendi@yahoo.com*

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**Abstract.** Waste of batik industry that is not well processed potentially contaminate the aquatic environment. Liquid waste concentration of 0%, 50%, 75%, and 100% was applied to vetiver (*Chrysopogon zizanioides* L.) grown in floating wetland system for treatment of batik industry liquid waste. Research was conducted in Akademi Kimia Analisis (AKA) Bogor, Indonesia. This study aimed to determine the ability of vetiver for reducing the concentration of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, TAN, BOD, COD, and total chromium. 50% of batik waste water was revealed to be the most suitable concentration treated by vetiver in floating wetland, since it could reduce not only ammonia, confirmed by biplot analysis, but also 40.29% total chromium concentration.

**Keywords:** *ammonia, batik, chromium, wastewater, wetland*

## Introduction

The batik industry in Indonesia has been progressing very rapidly, especially after UNESCO designated Indonesian batik as a Masterpiece of Oral and Intangible Heritage of Humanity on 2 October, 2009. Raw materials for batik production such as chemicals in the form of dyes and supporting materials such as water used in the washing and rinsing process, potentially become batik liquid waste. Batik is mostly produced in home industries that do not have wastewater treatment. The batik liquid waste is directly disposed to canals or rivers, causing a negative impact on the environment. There are two types of dyes used in batik product, namely natural and synthetic. Natural dyes include indigosol and remazol black B (Holkar et al., 2014) and synthetic dyes are nitroso, nitro, azo, stilben, diphenyl methane, triphenyl methane, acridine, kinolin, indigoida, aminokinone, anine and indophenol (Al-kdasi, 2004). Various metal complex dyes (chromium, cobalt, copper and nickel complex dyes) are widely used in textile industries as coloring agent (Aksu and Balibek, 2010). The use of chromium metal in the textile dyeing process will have an impact on the environment and cause poisoning in waters (Akar and Tunali, 2006). The presence of chromium in waters is found in two forms: chromium valence III (Cr<sup>3+</sup>) and Chromium VI (Cr<sup>6+</sup>) ions. Chromium valence VI is more toxic than Chromium valence III as it is difficult to decompose.

Phytoremediation is a cost effective and ecofriendly technique to clean contaminated soil and wastewater. Phytoremediation is the use of green plants including forb grass and wood species to remove environmental contamination such as heavy metals, trace

elements, organic compounds, and radioactive compounds in soil or water (Hegazy et al., 2011; Mojiri, 2012) to absorb pollutants. *C. zizanioides* exhibits good growth when grown on some types of wastes, such as fish farming wastes in aquaponic systems (Effendi et al., 2015a, b, c, 2016), crude oil contaminated waters (Effendi et al., 2017), tofu production wastewater (Seroja et al., 2018). It can improve the quality of the wastewater (Bedewe, 2010; Boonsong and Chansiri, 2008; Yeboah et al., 2015) and decrease Trichloroethylene (TCE) from contaminated soil by 98% (Janngam, 2010). In addition, *C. zizanioides* is able to absorb N and P (Darajeh, 2014), heavy metals, tolerant to herbicides and pesticides (Truong et al., 2010); to utilize tilapia cultivation waste (Delis et al., 2015), freshwater crayfish cultivation waste (Effendi et al., 2015b), and vaname shrimp aquaculture waste (Syafudin, 2015); lowering chromium content in mud (Rodríguez et al., 2010). The research aimed at using vetiver plant in reducing NH<sub>3</sub>, NH<sub>4</sub>, TAN, BOD, COD, and total chromium of batik liquid waste in floating wetland system.

## Materials and method

Liquid waste originated from batik industry in Jababeka Cikarang industrial area, Indonesia. Water quality analysis was conducted at the Laboratory of Environmental Test and Laboratory of Polytechnique of Akademi Kimia Analisis (AKA) Bogor. The study used *C. zizanioides* as a phyto-remediator plant. The treatments consisted of wastewater concentration of PL0 control (0% waste), PL50 (50% waste), PL75 (75% waste), and PL100 (100% waste) with triplicates. Into each batik liquid waste treatment was spiked Potassium dichromate as Cr<sup>6+</sup> to increase chromium concentration up to 2 ppm. Concentration of the added chromium content refers to the Regulation of the Minister of Environment No. 5 of 2014 on waste of batik and textile industry of 0.5-1 ppm.

*C. zizanioides* are washed and placed in a plastic tube stored in a container (25 L) of water and nutrient solution of A & B mix consisting of N, P, K, Mg, B, Cu, Mn, Mo, and Fe. Each container comprised of 6 pots containing 3 clumps vetiver of each pot. The plants were acclimatized for 3 weeks in floating wetland system where the roots were submerged in the water (Darajeh, 2014) before used.

Water quality parameters of temperature, Total Suspended Solid (TSS), pH, total ammonia (NH<sub>3</sub>), ammonium (NH<sub>4</sub>), Total Ammonia Nitrogen (TAN), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and total chromium (in water, root, leaf) were determined. Measurements were taken weekly, referring to APHA (2012). NH<sub>4</sub><sup>+</sup> (Eq. 1) and NH<sub>3</sub> (Eq. 2) concentrations were calculated as follows (Table 1) (Strickland and Parsons, 1972).

$$\text{NH}_4^+ (\text{mg/l}) = \frac{\text{TAN}}{1 + \text{antilog}(\text{pH} - \text{pKa})} + \quad (\text{Eq.1})$$

$$\text{NH}_3 (\text{mg/L}) = \text{TAN} - \text{NH}_4^+ \quad (\text{Eq.2})$$

**Table 1.** Value of pKa according to value of temperature

Temperature (°C)	5	10	15	20	25	30
pKa	9.90	9.73	9.56	9.40	9.24	9.09

Statistical analysis was performed using ANOVA followed by Duncan test ( $p < 0.05$ ). Correlation of Pearson and biplot analysis were also calculated using SAS software version 9.1.

## Results and discussion

Growth performance of vetiver as phytoremediator of batik production wastewater is elaborated in detail and published elsewhere (Tambunan et al., 2018). Below water quality improvement is described following remediation process, considering especially nitrogen concentrations (TAN,  $\text{NH}_4^+$ ,  $\text{NH}_3$ ) and chromium reduction. Initial characteristic of batik wastewater is presented in *Table 2*.

**Table 2.** Characteristics of inlet of batik wastewater (Tambunan et al., 2018)

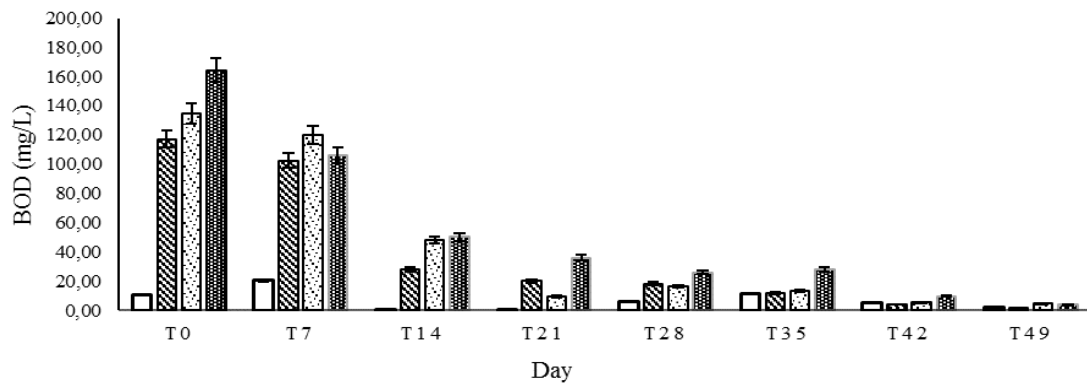
Parameter	Unit	Batik/textiles wastewater	Regulation of the Minister of Environment No 5, 2014
Temperature	°C	30	----
TSS	mg/L	268	50
pH	-	9.8	6.0 – 9.0
Total ammonia	mg/L	1.27	8.0
BOD	mg/L	966.83	60
COD	mg/L	2900.48	150
Total chromium	mg/L	2.34 (spike)	1.0

Temperature ranged from 28.10 to 29.10 °C. Based on statistical analysis, the temperature during the treatment was not significantly different, but observation time had significant effect on temperature ( $p < 0.05$ ). The pH ranged between 7.30-9.76, pH on day T0-T28 was not significantly different ( $p > 0.05$ ), however when compared with day T35-T49 it was significantly different ( $p < 0.05$ ). According to Singh et al. (2014) plants effectively absorbed waste at pH of 6-9. pH 7-8 is the optimal pH for vetiver in removing BOD, while at  $\text{pH} < 5$  vetiver performance in eliminating BOD ranged 10-40%. High pH (12) can inhibit vetiver performance (Darajeh, 2016).

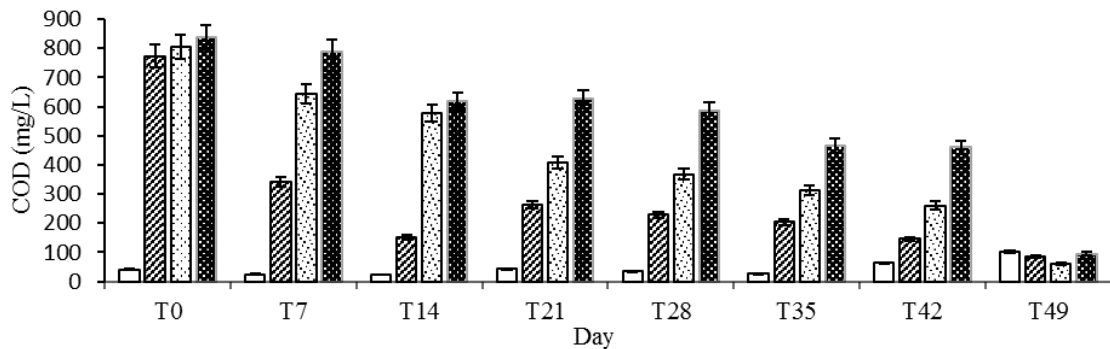
BOD in all treatments ranged 1.80 – 3.68 mg/L, meanwhile before treatment BOD was 117.28 mg/L (PL50), undergoing reduction (97.76-98.47%) after treatment. Each treatment and observation time had significant effect on BOD ( $p < 0.05$ ). *Figure 1* shows the fluctuations of the BOD during observation time. Drastic decline occurred on day T7 and T14, reducing BOD concentration occurred until T49. COD after treatment ranged 60.89-95.18 mg/L (initial range of 773.50-806.00 mg/L). Statistical analysis of each treatment and time of observation pointed out significant effect on COD ( $p < 0.05$ ). It is shown in *Figure 2* that from T0 to the end of the observation for each treatment, COD showed the same pattern of decline, but from T14 to T21 increased from 152 mg/L to 262 mg/L, followed by a subsequent decrease at the end of the observation.

Total Ammonia Nitrogen (TAN) consists of unionized ammonia ( $\text{NH}_3$ ) and ionized ammonia ( $\text{NH}_4^+$ ). Ammonia ( $\text{NH}_3$ ) is toxic to aquatic organisms, while ammonium ( $\text{NH}_4^+$ ) is harmless and it is in a form that plants can harness as a source of nutrient (Effendi, 2003). The percentage of  $\text{NH}_3$  in the waters decreased with decreasing pH and

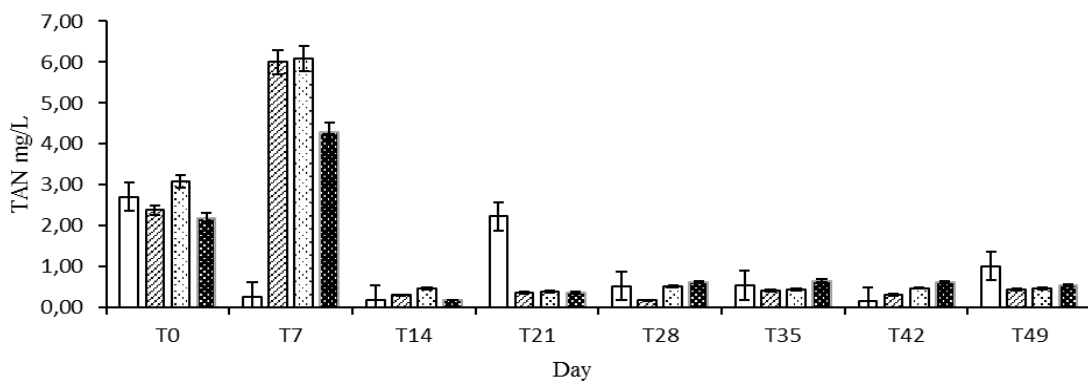
water temperature. TAN concentration increased from day T0-T7, then decreased drastically on day T14 (Fig. 3). Degradation of organic matter inhibits the rate of nitrification thus disrupting bacterial growth, inhibiting ammonia oxidation, and causing accumulation of TAN (Chen et al., 2005). Ammonia is water-soluble and very harmful to fish, and most tropical species that are generally more sensitive to ammonia (Effendi et al., 2015c; Wang and Leung, 2015). In this study the ammonia concentration increased on day 7, then decreased on day 14 drastically (Fig. 4).



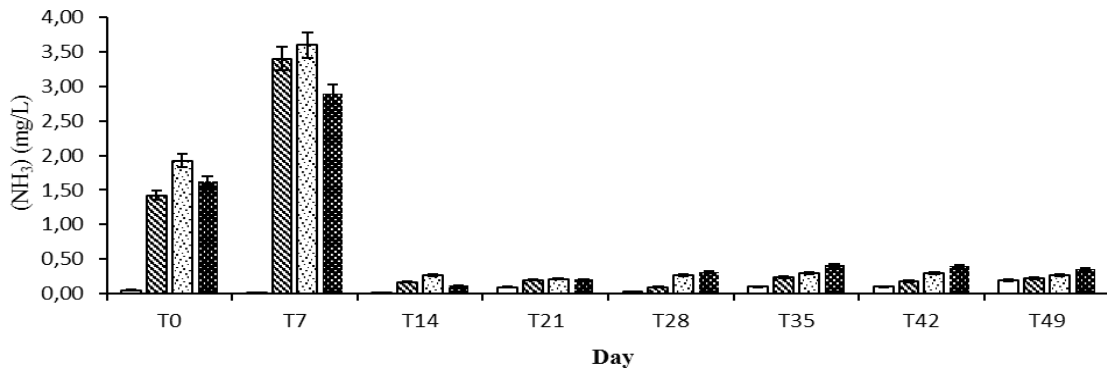
**Figure 1.** BOD decrease during the observation period. Description: □ PL0 (without waste 0%), ▨ PL50 (50% waste), ▩ PL75 (75% waste), ▧ PL100 (100% waste)



**Figure 2.** COD decrease during the observation period. Description: □ PL0 (without waste 0%), ▨ PL50 (50% waste), ▩ PL75 (75% waste), ▧ PL100 (100% waste)



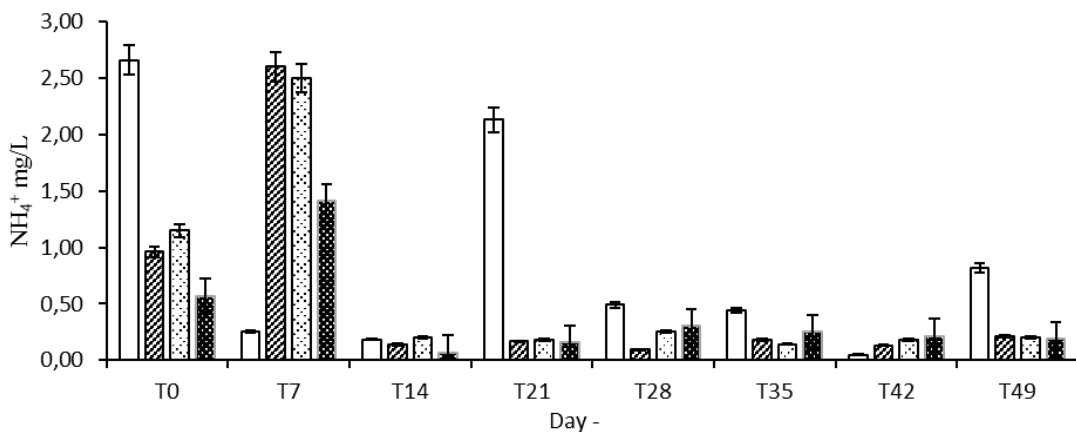
**Figure 3.** Total ammonia nitrogen (TAN) reduction during observation period. Description: □ PL0 (without waste 0%), ▨ PL50 (50% waste), ▩ PL75 (75% waste), ▧ PL100 (100% waste)



**Figure 4.** Ammonia reduction during observation period. Description: □ PL0 (without waste 0%), ▨ PL50 (50% waste), ▩ PL75 (75% waste), ■ PL100 (100% waste)

The NH<sub>3</sub> concentrations at the end of the observations for the PL0, PL50, PL75 and PL100 treatments were 0.19 mg/L, 0.22 mg/L, 0.26 mg/L, 0.35 mg/L, respectively. Initial total ammonia concentration was 1.42-1.92 mg/L. The NH<sub>3</sub> difference occurred at day 14. Percentage of NH<sub>3</sub> removal in each treatment of PL50, PL75 and PL100 was 84.51%, 86.47% and 78.14%, respectively. The results of this study are not much different from the research of Effendi et al. (2015b) of 84.6% NH<sub>3</sub> removal in freshwater lobster cultivation waste using kale, but this result is higher than the result of Delis et al. (2015) with NH<sub>3</sub> removal percentage of 31.3-48.36%, and Syafrudin et al. (2015) of 37.14-43.83% NH<sub>3</sub> removal in shrimp farming waste in wetland system.

Figure 5 shows the NH<sub>4</sub><sup>+</sup> concentration which increased on day 7, then decreased until day 49. Decreasing NH<sub>4</sub><sup>+</sup> during the experiment indicated that the vetiver could absorb and utilize NH<sub>4</sub><sup>+</sup>. High NH<sub>4</sub><sup>+</sup> fluctuations during the study were observed in PL0 (control), where day T0 and day T21 increased and decreased until day T49. The highest percentage of NH<sub>4</sub><sup>+</sup> degradation (82.57%) existed at PL75, greater than the result of research on shrimp farming waste in hydroponic system (Syafrudin et al., 2015).



**Figure 5.** Ammonium (NH<sub>4</sub><sup>+</sup>) reduction during observation period. Description: □ PL0 (without waste 0%), ▨ PL50 (50% waste), ▩ PL75 (75% waste), ■ PL100 (100% waste)

Percentage of TSS decreases at PL50, PL75, and PL100 were -38%, -49%, and -72% respectively, indicating that an increase of TSS took place (Table 3). This is likely due

to the addition of AB mix nutrients and remediation process with vetiver, so that TSS at the end of the observation (1183 mg/L) was greater than that at the beginning of the experiment (1673 mg/L). The higher the concentration of waste was the higher TSS concentration could be observed. The organic and inorganic compounds contained in the wastewater are bonded in suspended material (Effendi, 2003). Water quality parameters at PL100 generally had the smallest percentage of decline compared to those at PL50 and PL75.

**Table 3.** Reduction percentage of all water quality parameters of each treatment

Parameter	Unit	PL50		Reduction (%)	PL75		Reduction (%)	PL100		Reduction (%)
		Start	End		Start	End		Start	End	
TSS	mg/L	1183	1637	-38	1579	2346	-49	2127	3668	-72
pH	-	9.30	9.13	1.75	9.35	9.24	1.08	9.56	9.39	1.72
TAN	mg/L	2.38	0.44	81.69	3.07	0.46	85.01	2.19	0.54	75.52
NH <sub>4</sub> <sup>+</sup>	mg/L	0.96	0.56	77.50	1.15	0.60	82.57	0.57	0.39	67.17
NH <sub>3</sub>	mg/L	1.42	0.22	84.51	1.92	0.26	86.47	1.62	0.35	78.46
BOD	mg/L	117.28	1.80	98.47	134.77	2.52	98.13	164.21	3.68	97.76
COD	mg/L	773.50	84.72	89.05	806.00	60.89	92.45	788.64	95.18	88.65
Total chromium	mg/L	1.07	0.64	40.29	1.52	0.99	34.87	2.17	1.98	8.85

TAN at each treatment was significantly different, but ammonium (NH<sub>4</sub><sup>+</sup>) was not significantly different. Meanwhile, NH<sub>3</sub> concentration at PL0 was significantly different from NH<sub>3</sub> at PL50, PL75, and PL100. The percentage of NH<sub>3</sub> reduction for each treatment was PL50 (84.51%), PL75 (86.47%), and PL100 (78.46%). Fluctuation of TAN and ammonium at PL0 throughout the experiment might be related to the fact that the plant is naturally associated with bacteria living in its root submerged in the system.

The results of this study are still lower than the research using lettuce with percentage of NH<sub>3</sub> decrease of 90.1% (Effendi et al., 2015c), but higher than research using the combination of *Ipomea aquatica* and bacteria in the aquaponic system as much as 81% (Effendi et al., 2015d). Ammonia when discharged into the waters will disturb the life of aquatic biota such as fish (Effendi et al., 2015c). Meanwhile total chromium was significantly different in all treatments. In addition, total chromium reduction decreased with increasing waste concentration namely 40.29% (50% waste), 34.87% (75% waste), and 8.85% (100% waste). Bioremediation of chromium complex dyes in synthetic solutions and actual effluent was performed using growing *Aspergillus tamaris* in batch and continuous bioreactors. Maximum removal of chromium (94.00 ± 0.10 and 77.50 ± 0.10%) was obtained from synthetic solutions (100 mg/L) of acid brown 45 and acid blue 158 dyes, respectively in batch mode using *Aspergillus tamaris* (Ghosh et al., 2017). Chromium accumulation in root and leaf is presented in Table 4.

Plant growth parameters (clump, wet weight) correlated positively with nitrogen (TAN, NH<sub>4</sub>, NH<sub>3</sub>), BOD and COD with significant level of 0.05. This illustrated that plant might utilize nutrient resulting from organic substance decomposition. Meanwhile wet weight and Relative Growth Rate (RGR) correlated negatively with TSS (-0.761) and total chromium (-0.310), implying that both parameters disrupted the growth of plant (Table 5).

**Table 4.** Accumulation of Cr in vetiver (Tambunan et al., 2018)

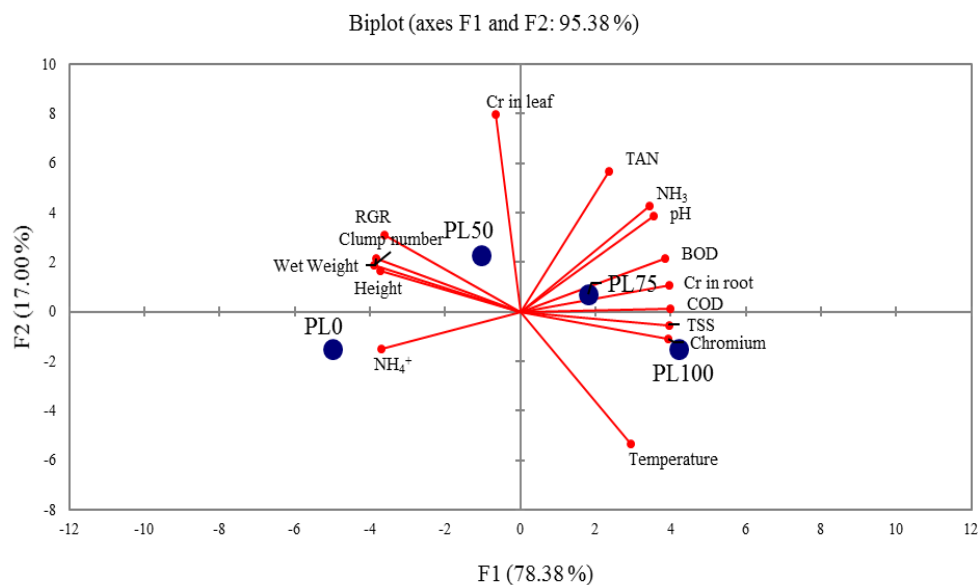
Parameter	Concentration (mg kg <sup>-1</sup> )			
	PL0	PL50	PL75	PL100
Root	0.45	18.28	27.17	33.52
Leaf	0.88	1.27	0.96	0.86
Total accumulation	1.33	19.56	28.12	34.37

Description: PL0 = vetiver control (*C. zizanioides*) without waste, PL50 = vetiver in 50% wastes + 50% water, PL75 = vetiver in 75% wastes + 25% water, PL100 = vetiver in 100% waste

**Table 5.** Pearson correlation analysis of each parameter

Parameter	Height	NH <sub>3</sub>	NH <sub>4</sub>	pH	Temp	COD	Total chromium	TSS	BOD	TAN	Clump	Wet weight	RGR
Height	1.000	-0.455	-0.299	0.081	-0.386	-0.633	-0.421	-0.040	-0.620	-0.487	-0.593	-0.219	0.936
NH <sub>3</sub>	-0.455	1.000	0.130	0.373	0.172	0.706	0.460	0.044	0.628	0.682	0.453	0.251	-0.423
NH <sub>4</sub>	-0.299	0.130	1.000	-0.597	0.231	-0.002	-0.309	-0.371	0.021	0.814	0.417	0.263	-0.263
pH	0.081	0.373	-0.597	1.000	-0.213	0.461	0.697	0.561	0.369	-0.221	-0.256	-0.211	0.052
Temp	-0.386	0.172	0.231	-0.213	1.000	0.199	0.147	-0.096	0.266	0.271	0.379	0.218	-0.266
COD	-0.633	0.706	-0.002	0.461	0.199	1.000	0.569	-0.023	0.903	0.413	0.687	0.420	-0.581
Total chromium	-0.421	0.460	-0.309	0.697	0.147	0.569	1.000	0.784	0.542	0.042	-0.054	-0.310	-0.500
TSS	-0.040	0.044	-0.371	0.561	-0.096	-0.023	0.784	1.000	-0.012	-0.247	-0.597	-0.761	-0.175
BOD	-0.620	0.628	0.021	0.369	0.266	0.903	0.542	-0.012	1.000	0.385	0.649	0.392	-0.573
TAN	-0.487	0.682	0.814	-0.221	0.271	0.413	0.042	-0.247	0.385	1.000	0.573	0.341	-0.441
Clump	-0.593	0.453	0.417	-0.256	0.379	0.687	-0.054	-0.597	0.649	0.573	1.000	0.775	-0.527
Wet weight	-0.219	0.251	0.263	-0.211	0.218	0.420	-0.310	-0.761	0.392	0.341	0.775	1.000	-0.133
RGR	0.936	-0.423	-0.263	0.052	-0.266	-0.581	-0.500	-0.175	-0.573	-0.441	-0.527	-0.133	1.000

The results of biplot analysis are shown in *Figure 6*.



**Figure 6.** Biplot analysis between each treatment and all parameters

Different treatments (PL0, PL50, PL75 and PL100) are illustrated by bold dots. These four points show the proximity of treatment with growth and water quality parameter. The parameters that have dominant proximity to PL0 and PL50 are mostly plant growth parameters (clump number, height, weight wet, RGR). This phenomena denoted that 50% waste was better for supporting the growth of plant compared to 75% and 100% waste. Meanwhile PL75 and PL100 were surrounded by water quality parameters (TAN, NH<sub>4</sub>, BOD, COD, pH, TSS, chromium in water), as consequences of larger concentration of waste. Conversely, growth of plants in the form of plant height, wet weight and number of clumps become lower with increasing concentration of waste, since those parameters were away from PL75 and PL100 in biplot analysis.

## Conclusion

In this particular research, 50% of batik waste water treated by vetiver in floating wetland was revealed as the most suitable concentration, resulting in better water quality parameter reduction, and total ammonia concentration reduction.

This research result provides simple promising biological treatment of batik production wastewater instead of chemical treatment. The application of this research in batik production wastewater location will soon be pursued.

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