Effectivity of *Vetiveria zizanioides* and *Cyperus papyrus* in Reducing Iron (Fe) Concentration in Wastewater Processed in a Constructed Wetland System

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***Abstract*—**Iron (Fe) and iron-containing compounds are used in various industries and thus Fe production in the world has reached more than 500 million tons per year. The use of Fe in various industrial processes and its high presence in the environment can potentially pollute water bodies and be toxic to aquatic biota. The application of constructed wetland systems provides an alternative approach to treat this problem. This study was conducted to examine the effectiveness of a surface flow constructed wetland system, planted with *Vetiveria zizanioides* and *Cyperus papyrus*, in reducing Fe concentration in simulated wastewater. Experimental systems were exposed to artificial wastewater containing $FeSO_4.7H_2O$, equivalent to 60 ppm Fe concentration. Each experimental run was conducted for 18 days by comparing five different systems: system-A as control contained only wastewater; system-B contained wastewater and substrate; system-C contained wastewater, substrate and planted with *V. zizanioides*; system-D contained wastewater, substrate and planted with *C. papyrus*; while system-E contained wastewater, substrate, and planted with both *V. zizanioides* and *C. papyrus*. Measurements were conducted on Fe concentration and physical-chemical parameters of wastewater, substrate and air. Results indicate that system-C was most effective in decreasing Fe concentration to reach the maximum allowable concentration (MAC) (20 ppm) when compared to the other systems. On the sixth day of treatment, Fe concentration in system-C reached 16.2 ppm, i.e., a reduction percentage of 70%. On the same day, Fe concentration in system-E measured 16.6 ppm (69% reduction). System-D and system-B reached the permitted level on the ninth day with reduction percentage of 62% and 61% respectively. Meanwhile, as control, system-A was the slowest in decreasing Fe concentration; on the twelfth day, Fe concentration reached 18.1 ppm, i.e., a reduction of 65%. Statistical analysis showed that there was a significant difference among systems in Fe concentration reduction in wastewater on the sixth to fifteenth day of observation ($p < 0.05$). Results of this study indicated that the addition of *V. zizanioides* and *C. papyrus* can improve system effectiveness in reducing Fe concentration.

***Keywords*—**Constructed wetland, Fe concentration, *Vetiveria zizanioides*, *Cyperus papyrus*

I. Introduction

Metallic iron (Fe) and its compounds are used in various industries, including pharmaceutical, chemical, fertilizer and pesticides, textile, automotive, and construction industries. To meet these needs, the production of Fe in the world has reached more than 500 million tons per year. In addition, Fe compounds can also be formed as a result of various activities such as mining [1].

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The use of Fe in a variety of industries results in a high probability of this element contaminating aquatic ecosystems. Water bodies that have been contaminated with Fe may have a pH range between 2.0 to 4.5 which is toxic to aquatic life. These low pH values will disrupt the growth and reproduction of aquatic biota [2]. Studies have also cited that low pH conditions can alter gill membranes resulting in fish death due to hypoxia. Particulate Fe sediment that covers the surface of river and lake sediment can also disrupt the availability of clean gravel that serves as spawning sites and reduce benthic macroinvertebrates numbers as fish food. Therefore, Fe compounds that pollute water bodies will damage aquatic habitats biologically, physically and chemically [3].

The application of constructed wetland systems is one approach to addressing the problem of metal contamination, including Fe. Constructed wetland systems have been developed for wastewater treatment. In the working principle of constructed wetlands, pollutants in the system will encounter sedimentation, precipitation, adsorption to soil particles, assimilation by plant tissues, and transformation by microbes. In other words, pollutants contained in wetland systems will be treated through a series of physical, chemical and biological processes [4]–[8].

Wetland plants are important components of wetland ecosystems because of their role in the process of sewage treatment [8]. Amongst various species, *Vetiveria zizanioides* and *Cyperus papyrus* are often used for phytoremediation purposes because these plants are able to respond to alteration of long term water levels and have good adaptability in extreme environmental conditions [9]–[11]. The following study was conducted to examine the effectivity of a free water surface wetland planted with *V. zizanioides* and *C. papyrus* in reducing Fe concentration in wastewater.

II. Methodology

Experimental constructed wetland systems with free water surface were made from glass aquariums measuring 60 cm in length, 30 cm in width and 30 cm in height. Five different systems were compared in this study. System-A as control only contained simulated wastewater containing Fe (coded: w+Fe); system-B contained wastewater and substrate (w+Fe+S); system-C contained wastewater, substrate and planted *V. zizanioides* (w+Fe+S+V); system-D contained wastewater, substrate and *C. papyrus* (w+Fe+S+Cy); finally, system-E contained wastewater, substrate, and planted with both *V. zizanioides* and *C. papyrus* (w+Fe+S+V+Cy). Experiments were replicated three times. Simulated wastewater treated into each system was made by dissolving 10.5 g $FeSO_4.7H_2O$ in 35 L of distilled water in order to obtain Fe concentration of 60 ppm. Wastewater was flowed into the systems through an inlet point, then wastewater flowing out of the outlet point was collected in a container before being recirculated into the inlet point (Fig. 1). Retention time for each circulation was 15 minutes, as determined by equation (1) [12].

$$t = \frac{System\ Volume\ (L)}{Water\ Discharge\ (\frac{L}{minute})} \qquad (1)$$

Each experimental run was conducted for 18 days. Measurements of Fe concentrations in wastewater, substrate and roots of plants, as well as physicochemical conditions of wastewater and substrate were carried out every three days.

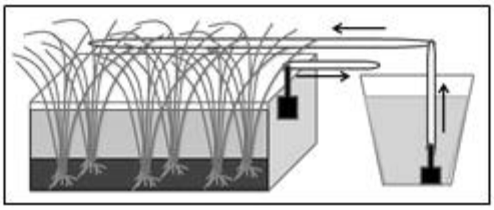

Fig. 1. Constructed wetland system used in this study.

Physical and chemical parameters of wastewater measured include pH, TDS (total dissolved solids), TSS (total suspended solids) and Fe concentration. These parameters were measured using pH meter for pH, TDS meter for TDS, TSS meter for TSS, and atomic absorption spectrophotometer (AAS) for Fe concentration. Physical and chemical parameters of substrate measured include pH using pH tester and Fe concentration by AAS analysis.

Wet ashing method was used for the preparation of wastewater, substrate and plant root samples before analysis for Fe concentration. Fifty mL each of wastewater samples, 1 g of substrate samples and 3 g of plant root samples that have been dried at 80^{0}C were dissolved in 50 mL HNO_3. In the next step, samples were kept in the hood for 12 hours and then heated at 125^{0}C for 45 minutes. After cooling at room temperature, samples were added with 1 mL of H_2O_2 30% and re-heated at 125^{0}C temperature for 45 minutes. Addition of H_2O_2 30% and heating at temperature of 125^{0}C were continued until samples appeared clear [13]. Sufficient HNO_3 was added to the samples in order to measure Fe concentration using AAS at a wavelength (λ) of 248.3 nm [14].

III. Results And Discussion

Measurement results show a decrease of Fe concentration in wastewater processed by the systems tested (Fig. 2). From the five treatments, system-C and system-E reduced Fe concentrations faster than the other treatments.

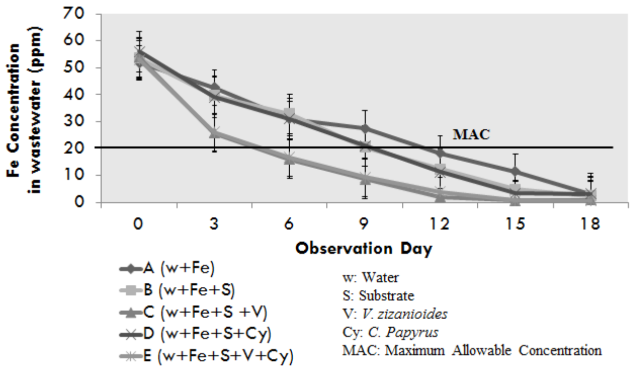

Fig. 2. Fe concentration in wastewater.

Measurement results also indicate increasing Fe concentrations in substrate of the four systems containing substrate (Fig. 3). Fe concentrations in system-C and system-E showed a high increase on the 3rd day until the 12th day of observation. These results may be related to the presence of *V. zizanioides* in system-C and system-E. The morphology of *V. zizanioides* is very appropriate to select as a constructed wetland plant because it has stiff stems and forms dense hedges to restrict pollutant movement. This condition greatly enhances the process of pollutant sedimentation [15].

On the 12th until 18th day of observation, Fe concentrations in substrate of systems planted with vegetation (system-C, system-D and system-E) showed reduction. This reduction may be related to the accumulation of Fe from substrate in plant root areas. In system-B which was not planted with vegetation, sedimentation of Fe compounds merely occurred due to substrate, causing Fe concentration in the system to increase up to the 18th day of observation.

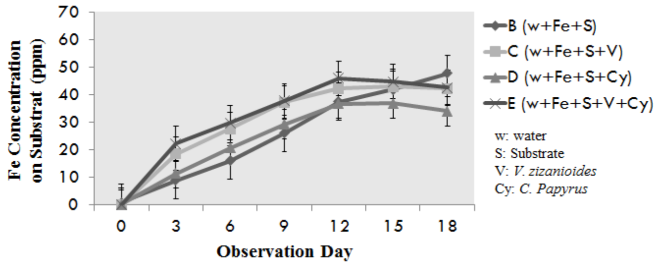

Fig. 3. Fe concentration in substrate.

From the graph of percent decrease in wastewater Fe concentration (Fig. 4), it can be seen that Fe concentrations decreased by 90% within 18 days in all systems.

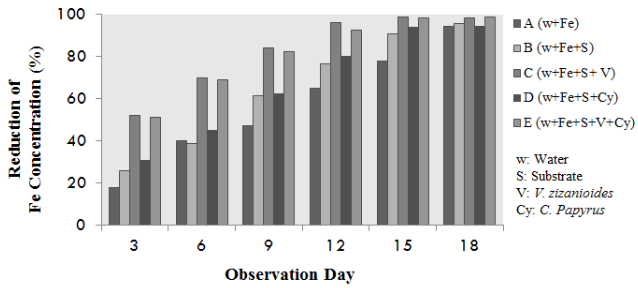

Fig. 4. Percentage of Fe concentration reduction in wastewater.

However, each system reached the Fe maximum allowable concentration (MAC) of 20 ppm at different times (Table 1). System-C reached MAC most effectively and in the shortest amount of time, while system-A as control needed the longest amount of time. Statistical analysis showed that there was a significant difference among systems in reducing concentrations of Fe in wastewater on the 6th day of observation until the the 15th day of observation (p <0.05).

TABLE I: ACHIEVEMENT OF MAXIMUM ALLOWABLE CONCENTRATION (20 PPM)

System	Observation day	Fe Concentration (ppm)	Percentage (%)
A (w+Fe)	12th	18.1 ± 0.7	65
B (w+Fe+S)	9th	20.6 ± 2.1	61
C (w+Fe+S+V)	6th	16.2 ± 5.5	70
D (w+Fe+S+Cy)	9th	21.1 ± 3.7	62
E (w+Fe+S+V+Cy)	6th	16.6 ± 4.3	69

The presence of vegetation in a constructed wetland system does not only optimize the process of sedimentation but also absorbs heavy metal [16]. Measurement results (Fig. 5) indicate increasing Fe concentrations around plant root areas after treated. However, this escalation was not statistically different among systems ($\alpha = 0.05$; $p = 0.961$).

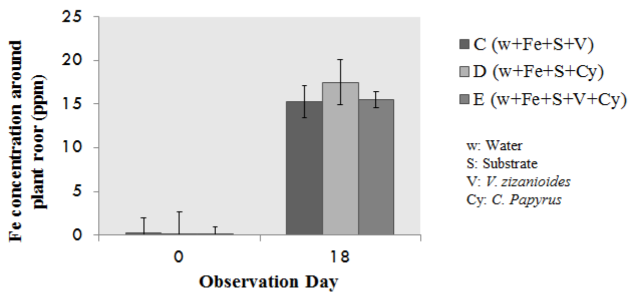

Fig. 5. Fe concentration around plant root areas.

Wetland plant roots are the first organ that plays a role in heavy metal absorption. The first stage is phytoaccumulation, which is the accumulation of pollutants from growth media to the root. The next is rhizofiltration which is an adsorption process or deposition of pollutants to cling around the roots. The next stage is phytostabilization in which pollutants that cannot be absorbed into the stem become attached to the roots. Attachment of these substances is very strong and stable, thus it will not be carried away by the flow of water in the media. The next stage is known as rhizodegradation which is the decomposition of pollutants around roots with the help of microbes. The last stage is phytodegradation or phytotransformation [17].

The process of wet ashing of plant roots in this study followed Plank's method [13]. In wet ashing, roots were only cleaned from soil particles. Therefore, results of Fe concentration measurements in root samples could not be assumed to be entirely Fe absorbed into the roots. However, measurements are assumed to be accumulated around the root area and will be absorbed by the roots. From the literature it is known that heavy metals accumulate around roots before they can be absorbed by the roots [17].

Fe is a plant micronutrient that is needed in small amount. This element is a constituent of cytochrome and non-heme iron protein involved in photosynthesis, N_2 fixation and respiration. Fe present in the substrate is absorbed by roots through the root apex or directly through the root surface. After Fe is absorbed by the roots, it will oxidize to ferric form and translocate to the leaves [18].

Water pH value is an important parameter of water that determines the solubility and availability of nutrients, including metals such as Fe. Solubility refers to the amount of substance that dissolves in water. $FeSO_4.7H_2O$ solubility in water will rise at low pH. Fe is dissolved in water in the form of ferrous ions which will be oxidized to become particulate and precipitate [19].

Measurement results (Fig. 6) show that wastewater pH at the beginning of the treatment was very low. In this condition, the solubility of ferrous ions from $FeSO_4.7H_2O$ compound was higher compared to the end of experimental treatment.

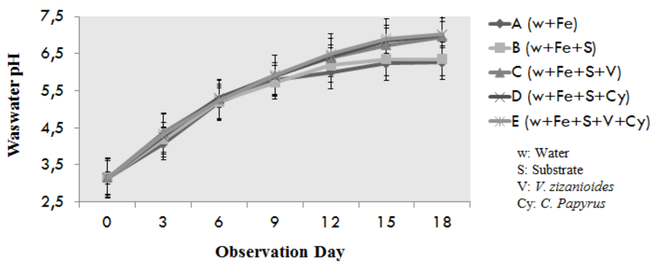

Fig. 6. Wastewater pH

Wastewater pH value continued to increase until the 18th day of observation. The increase in wastewater pH is associated with the solubility reduction of iron compounds in wastewater due to sedimentation; thus measurements indicate a decrease in substrate pH (Table 2).

TABLE 2: SUBSTRATE PH (WITHIN A COLUMN, DIFFERENT LETTERS INDICATE SIGNIFICANT DIFFERENCE AT P < 0.05)

System	Before treatment	After treatment
B (w+Fe+S)	$(6.4 \pm 0.1)^a$	$(3.9 \pm 0.1)^b$
C (w+Fe+S+V)	$(6.4 \pm 0.1)^a$	$(3.9 \pm 0.1)^b$
D (w+Fe+S+Cy)	$(6.4 \pm 0.1)^a$	$(4.0 \pm 0.1)^{bc}$
E (w+Fe+S+V+Cy)	$(6.4 \pm 0.1)^a$	$(4.2 \pm 0.1)^c$

Results of TSS and TDS measurements in wastewater showed that the decrease of TSS and TDS concentrations was followed by decreasing Fe concentrations in wastewater. From the literature, it is known that suspended and dissolved material in water include carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, and other ions including ferrous ions, dissolved metals and pathogens [20]. Although TSS and TDS measurements cannot indicate exactly the concentration or changes of material in the water, TSS and TDS concentrations are parameters that must also be considered in monitoring water quality, including wastewater [20].

Therefore, the mechanisms that occurred decreasing Fe concentration in this study involve three main processes, i.e., chemical, physical and biological. Chemical processes occurred when ferrous ion from $FeSO_4.7H_2O$ dissolved in water underwent oxidation to form ferric ions. Ferric ion is a particulate form with low solubility in water, resulting in physical processes that precipitate particulate Fe to substrate [8][19]. Meanwhile, biological processes involved the plant's role in the system. In addition to retarding the water flow, wetland plants also absorb pollutants present in the system [16].

IV. Conclusion

The five constructed wetland systems that were varied based on the presence of substrate and plants were effective in reducing Fe concentrations to reach the maximum allowable level of 20 ppm after 18 days of treatment. However, the addition of *V. zizanioides* and *C. papyrus* could improve system effectivity by decreasing Fe concentration in a shorter time period.

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