PRELIMINARY TEST OF MINING WASTEWATER CONTAINING IRON (III) AND ALUMINIUM (III) ON *Scirpus grossus* IN PHYTOREMEDIATION PROCESS

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Abstract. Preliminary test was conducted to physically observe and determine the range of Fe and Al concentrations that *Scirpus grossus* can grow and survive. Pails of 3 L containing 3 kg of sand and 42 days old *S. grossus* were exposed to different concentrations of Fe and Al solution mixture for 21 days. The mass ratio between Fe and Al in the solution mixture was 3:1. After 21 days of exposure, the plants had shown that they could grow and survive in concentrations up to 300 mg/L Fe + 100 mg/L Al. Effect concentration (EC₅₀) value for single Fe and Al toxicity to *S. grossus* was predicted between 300 mg/L Fe + 100 mg/L Al and 450 mg/L Fe + 150 mg/L Al. Therefore, it is suggested for the next study of phytotoxicity the Fe and Al concentrations range may start as low as 30 mg/L Fe + 10 mg/L Al up to 450 mg/L Fe + 150 mg/L Al.

Introduction

Heavy metals may enter the environment through several points of sources either naturally through weathering, erosion of parent rocks, atmospheric deposition and volcanic activities or anthropogenic activities such as mining, smelting, electroplating, sewage irrigation, addition of manures, widely use of fertilizers and pesticides [1,2]. Heavy metals are natural constituents of the Earth's crust and they are stable and cannot be degraded or destroyed [3]. They tend to accumulate in soils, water and sediments [4]. Among those, mining is responsible for heavy metal contamination [5].

In this study, an active mining area near Tasik Chini, Pahang was selected as a study area. The mineral being removed is bauxite. Bauxite mining can lead to iron and aluminium contamination to the environment since the ores are mainly composed of Al₂O₃, SiO₂, Fe₂O₃ and TiO₂ [6] at which the mass ratio between these compounds are different in every country and also different in different region in a country [7]. It can happen naturally (i.e. rain) and also due to human (i.e. mining activity). The conversion of iron to ferric hydroxide precipitate can generate toxic derivatives and this will lead to infection, neoplasia, cardiomyopathy, arthropathy, and various endocrine and neurodegenerative disorders in human [8]. Likewise, aluminium also has the toxic influences which will lead to Parkinson's dementia, amyotrophic lateral sclerosis and Alzheimer's disease [9].

Due to the toxicity effects of the metals, many treatments being applied to reduce the concentrations of heavy metals below the allowable limits. Conventional treatment methods on heavy metals involved for water are reverse-osmosis, ion exchange, electrodialysis, adsorption by activated carbon, chemical precipitation, disinfection and nanofiltration [10,11,12]. However, those

treatments are generally costly, labour-intensive, can generate secondary waste or sludge, energy intensive and metal specific [4,12]. Therefore, a cost effective and environmental friendly approach [13,14] method like phytoremediation should be featured. Phytoremediation is a remediation method at which plant plays an important role to extract, degrade, contain or immobilize pollutants in soil, groundwater, surface water and other contaminated media [15]. It involves several mechanisms which are rhizofiltration, phytostabilization, phytotransformation, phytoextraction and phytovolatilization. In this study, a native plant of *Scirpus grossus* in Tasik Chini, Pahang was used. It has the ability to remediate iron and aluminium from contaminated areas since it was found in bauxite mining areas in Sungai Jemberau, Tasik Chini, Pahang [16]. It is a perennial tropical aquatic plant with common names of giant bulrush, greater club-rush, *rumput menderong* (Malaysia), *mensiang* and *walingi* (Indonesia) [17]. The objective of this test was to estimate the maximum concentration of the mixture of Fe (III) and Al (III) that the *S. grossus* has the ability to survive and tolerate. The results from this study can be used in future phytotoxicity study.

Materials and Methods

Propagation of *S. grossus* and preparation of synthetic mining wastewater. *S. grossus* was planted in garden soil which contain top soil, organic fertilizer i.e. cow manure and sand with ratio of 3:2:1. About 18 healthy plants of *S. grossus* with 42 days old were exposed to various mixture concentrations of Fe and Al. Before the preliminary test was conducted, the analysis of soil mining collected from Tasik Chini was done in order to determine the mass ratio between iron and aluminium. From the analysis, it was found that the mass ratio of Fe and Al was 3:1 [16]. The result from this analysis was used during the preliminary test of *S. grossus*. Stock solutions of Fe and Al were prepared separately by dissolving iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Friendemann Schmidt, U.K) and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$) (R & M Marketing, U.K) in distilled water. The dilutions for both stock solutions were done according to the required mixture concentration as in Table 1.

Table 1 Concentration of heavy metals in a pail and its function

Pail no.	Pail 1	Pail 2	Pail 3	Pail 4	Pail 5	Pail 6
Concentration of heavy metals in a pail						
[mg/L Fe]	0	150	300	450	600	750
[mg/L Al]	0	50	100	150	200	250
Function	PC	C1	C2	C3	C4	C5

PC= Plant control

C1– C5= Contaminant 1- Contaminant 5

Preparation of experimental setup. 3 kg of sand was filled in 3 L pail which was used as the batch reactor. Subsurface flow system was used since it was proven that it was more efficient than free surface flow system [18]. The duration of this test was 21 days. The physical observations of plants were observed on Day 0 and Day 21. At the end of the observation day, the percentage of cumulative effect was calculated using Eq. 1.

$$\text{Cumulative effect, \%} = \frac{\text{number of died plant}}{\text{number of total plant}} \times 100 \quad (1)$$

Quantitative description on plant growth. The plant growth of *S. grossus* was physically observed throughout the sampling period either healthy (overall leaves were green), withered (some leaves changing color to yellow) or died (the whole leaves were brown and dried).

Results and Discussion

Table 2 summarizes the physical observation of *S. grossus* on Day 0 and Day 21. Based on the plant growth observation, *S. grossus* remained healthy until the end of experimental period for PC. But, all three plants were dead for C3, C4 and C5. For C1 and C2, only one plant was died. The number of plants died increased as the concentrations of the Fe and Al increased. The dead of *S. grossus* was due to the Fe and Al toxicity which was also reported by many researchers due to the growth inhibition either in the roots or towards the upper part of the plants [19,20,21]. Fig. 1 depicts the effect concentration (EC_{50}) value for single Fe and Al toxicity to *S. grossus* which was predicted between 300 mg/L Fe and 100 mg/L Al to 450 mg/L Fe and 150 mg/L Al.

Fig. 1 Fe and Al toxicity to *S. grossus* at the end of exposure period

Based on the observations, the higher the concentration of Fe and Al, the greater the effect percentage and the faster died conditions occurred. Therefore, it is suggested for the future study of phytotoxicity can use Fe and Al concentrations range as low as 30 mg/L Fe + 10 mg/L Al up to 450 mg/L Fe + 150 mg/L Al.

Summary

The results showed that as the concentrations of the mixture of Fe and Al increased the withering symptoms and plant death also increased in parallel reducing the survival of *S. grossus*. After 21 days of exposure, the plants had shown that they could grow and survive in concentrations up to 300 mg/L Fe + 100 mg/L Al with survival percentage of 66.7. EC_{50} value for single Fe and Al toxicity to *S. grossus* which was predicted between 300 mg/L Fe + 100 mg/L Al to 450 mg/L Fe and 150 mg/L Al. Therefore, the future phytotoxicity study can start from 30 mg/L Fe + 10 mg/L Al until 450 mg/L Fe + 150 mg/L Al.

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Table 2 Plant physical observation during preliminary test for *S. grossus*

Time of exposure (Day)	Heavy metals concentration					
	0 [mg/L Fe] + 0 [mg/L Al]	150 [mg/L Fe] + 50 [mg/L Al]	300 [mg/L Fe] + 100 [mg/L Al]	450 [mg/L Fe] + 150 [mg/L Al]	600 [mg/L Fe] + 200 [mg/L Al]	750 [mg/L Fe] + 250 [mg/L Al]
	PC	C1	C2	C3	C4	C5
00	All plants were healthy	All plants were healthy	All plants were healthy	All plants were healthy	All plants were healthy	All plants were healthy
21	All plants were healthy 7 saplings	2 plants were healthy but 1 plant was died 3 saplings	2 plants were healthy but yellowish at the end of the leaves 1 plant was died 4 saplings	All plants were died	All plants were died	All plants were died

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