Effectiveness of Phytomining of Vanadium (V) and Chromium (Cr) Using *Cymbopogon citratus* and *Portulaca grandiflora* in Red Mud with Manure Addition

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Abstract. The highly alkaline nature of red mud, coupled with the presence of heavy metals, represents a significant environmental risk. Phytomining has the potential to facilitate the extraction of heavy metals, including vanadium (V) and chromium (Cr), from red mud. In this study, phytomining employs the use of *Cymbopogon citratus* and *Portulaca grandiflora* plants. The objective of this study is to evaluate the capacity of both plants to engage in phytomining and extract valuable metals from red mud. The methodology employed in this study entails the incorporation of stimulants in the form of manure at concentrations of 0%, 5%, and 10%. The study was conducted over a period of 28 days, during which time toxicity testing and the phytomining ability of the two plants were observed. The phytomining capacity of the plants was determined by measuring the concentration of vanadium (V) and chromium (Cr) in the plant extractions using inductively coupled plasma-optical emission spectroscopy (ICP-OES) equipment. The findings indicated that the *Cymbopogon citratus* and *Portulaca grandiflora* plants were capable of surviving on a red mud medium with the addition of 10% manure. The highest absorption of V metal was observed in *Cymbopogon citratus*, with a value of 23.3 mg/kg, when 10% manure and 90% red mud were added. The highest absorption of Cr metal was 18.02 mg/kg by *Portulaca grandiflora* with the addition of 10% manure and 90% red mud. Therefore, the results demonstrated that the addition of 10% manure enhanced the capacity of plants to absorb metals.

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1 Introduction

Red mud is an insoluble residue in the bauxite mining process which amounts to 120 million tons per year [1]. The amount of red mud is proportional to the high bauxite reserves of Indonesia and the world and is in the stage of comprehensive exploitation. However, it is a disadvantage that the process of mining and extracting bauxite ore is carried out openly [2]. In addition, some studies indicate the contents of metals and heavy metals aluminum (Al), iron (Fe), cuprum (Cu), manganese (Mn), lead (Pb), zinc (Zn), and arsenic (As) at levels exceeding the recommended content limits [3]. The content of these heavy metals makes red mud characterized by a pH that tends to be alkaline. The tendency of alkaline pH is also influenced by the Bayer process in producing aluminum from bauxite ore which uses sodium hydroxide as a solution agent [4].

The above conditions indicate that red mud requires specific handling to treat and remediate it. As time evolved and science and technology developed, the goal of environmental improvement has evolved to become profit-oriented. This transition will have an impact on the economic valuation of environmental effects on industry and the local area. The context of red mud itself as a residue from bayer process threatens ecotoxicity from the presence and release of metals and metalloids such as vanadium, chromium and molybdenum into the environment as occurred in 2010 in Ajka (Hungary) [5]. As much as 70-80% of the world's scandium is in bauxite mines [6]. Conditions, where these Rare Earth Element (REE) metals are only released into the environment, can only be called waste and cannot take advantage and profit.

Based on the above statement, the greatest potential is to conduct phytomining on Vanadium (V) and Scandium (Sc) metals which are expected to have sufficient concentrations to be uptaken using plants. Phytomining is an “environmentally friendly” metal mining method because it uses plants as a heavy metal uptake medium so it has a low environmental impact compared to open pit mining [7]. As a very low-cost technology, phytomining can potentially allow low-grade ores or mineralized soils to be economically exploited with too little metal for conventional mining [8].

Vanadium and Scandium metals are uptake planned using two plant species, *Cymbopogon citratus* and *Portulaca grandiflora*. Several studies have shown that both plant species are effective in dealing with metal-containing soils and heavy metals. *Cymbopogon citratus* has a high metal tolerance index (MTI) of 114.3%, indicating its ability to survive high metal exposure and remediate it [9]. MTI is a value used to measure a plant's resistance to metal exposure and accumulation. *Portulaca grandiflora* was able to absorb up to more than 40% of Fe and Al and more than 30% of Pb and Zn over 30 days [10]. Both plants have passed screening in determining the right plants for the phytomining process to be carried out.

Despite the high MTI value, the characteristics of the red mud to be remediated must be considered. Research reveals that fresh red mud with an age below five years will be difficult to remediate due to conditions that do not support plants to grow [9]. Therefore, in this study, the addition of manure fertilizer will be carried out to support plant life. The addition of fertilizers is often done in phytoremediation and phytomining research. O'Dell in [11] showed that the application of manure fertilizer in the phytomining process can reduce the biotoxicity of heavy metals, and accelerate plant growth. Based on the study, the addition of 2% manure to chromium (Cr) contaminated soil contributed to an almost two-fold increase in Solanum lycopersicum biomass in stems and roots [12].

In this research, redmud from West Kalimantan was used for phytomining metal. The purpose of the study is to determine the effectiveness of *Cymbopogon citratus* and

Portulaca grandiflora in the absorption of V and Cr from red mud. Furthermore, the addition of manure fertilizer as a stimulant and reduce toxicity.

2 Materials and method

2.1 Sample collection

The red mud used as media is from Tayan Subdistrict, Piasak Tayan Hilir Village, Balai Belungai, Toba District, Sanggau Regency, West Kalimantan, Indonesia, which was obtained from PT Indonesia Chemical Alumina in 2024. The map in Figure 1 shows the red mud sampling locations.

Fig. 1. Red mud sampling location

Meanwhile, manure was procured from a florist in Bratang Surabaya. Subsequently, the media preparation stage was undertaken, comprising the following steps.

1. The red mud was dried under direct sunlight for approximately 12 hours to facilitate the mixing process with manure. This natural drying process utilising the sun's heat was chosen to ensure that the scandium metal present in the red mud remained intact. The temperature generated by the sun, usually ranging from 30-40°C, is low enough to prevent the evaporation of scandium, which has a boiling point of 1.541°C.
2. The dried red mud is levelled and smoothed using tools such as shovels and hammers. This process is done to ensure a uniform consistency of the red mud particles.
3. Before mixing, the dried red mud and manure were sieved with a 10 mesh sieve. This process ensures that the particles of both materials are uniform in size, resulting in a homogeneous mixture and consistent distribution of the red mud and manure components throughout the media.

Upon completion of the preparation process, the red mud and manure was then mixed with three different ratios, namely 100:0, 19:1, and 9:1

2.2 Phytomining experiment

Once the growing medium was prepared, the reactors were configured for the initiation of the study.The research reactors comprised pots with a diameter of 16 cm and a height of 10 cm for *Cymbopogon citratus*, and a diameter of 12 cm and a height of 9 cm for *Portulaca grandiflora*. The research was conducted in duplicate with 18 reactors. The composition of the planting media mixture comprised three variations: 100% red mud and 0% manure, 95% red mud and 5% manure, and 90% red mud and 10% manure. The primary research was conducted for 28 days, with three tests of pH and electrical conductivity (EC) on days 0, 14, and 28. Soil pH and EC parameters were measured to determine fluctuations in pH and EC values as a tool to test hypothesis regarding the properties of red mud.

2.3 Metal extraction method

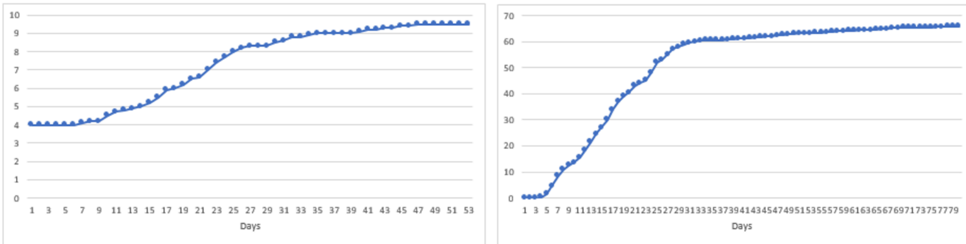
Following a 28-day period of the primary study, an analysis of heavy metals was conducted on the plants using an aqua regia solution. The analysis of heavy metals will be conducted on media samples using ethylenediaminetetraacetic acid (EDTA) solution to identify bioavailable heavy metals and aqua regia solution (5 HNO_3 : 1HCl) to determine the total bioavailable and non-bioavailable heavy metals. The preparation of media with aqua regia is in accordance with the standards set forth in SNI 8910:2021 [8].

3 Results and discussion

3.1 Plant propagation

The propagation stage is the phase during which plants are cultivated and bred. The process of multiplying plants at this stage is beneficial for preparing the requisite number of plants for phytomining. During this phase, physical observations of the plants are conducted, including measurements of stem height and an assessment of root conditions. Plant propagation is carried out for a minimum of one month until the plant reaches an optimal size for further treatment [13].

In the case of *Cymbopogon citratus*, the propagation stage is carried out by planting stems of the same height (approximately 15 cm) in order to facilitate the propagation of the plant. The generative period of the plant commences on day 27, characterised by the emergence of new branching shoots. By the 27th day, the plant had reached a height of 55 cm. This data serves as a reference point, indicating that the plant to be used is approximately 27 days old and 55 cm tall. With regard to *Portulaca grandiflora*, the procedure entails planting the stem into the garden soil. The length of the planted stem is 4 cm. The generative period of this plant begins on the 36th day with the growth of flowers. The plant height on the 36th day reached 9 cm. The following is a graph of the growth rate of *Cymbopogon citratus* and *Portulaca grandiflora*, shown in Figure 2.



(a) (b)

Fig. 2. Growth rate of (a) *Cymbopogon citratus* and (b) *Portulaca grandiflora*

3.2 Toxicity testing

A toxicity test was conducted on *Cymbopogon citratus* and *Portulaca grandiflora* with the objective of determining the minimum level of stimulants that could be added to red mud without causing adverse effects. The objective is to facilitate its application in the field, given the extensive hectares of red mud landfill. Consequently, the lower the level of stimulant added, the more feasible it is to apply the research in the field.

The experimental design entailed the calculation of various toxicity values, including LOEC, NOEC, LC50, and MATC.LOEC, or the lowest observable effect concentration, signifies the minimal substance concentration capable of eliciting a statistically significant toxic effect in test organisms, as compared to the control group. Conversely, NOEC, representing the highest concentration of a substance that does not cause a statistically significant toxic effect compared to the control, serves as a benchmark for safety assessment. The LC50 value indicates the concentration of a substance that results in mortality in 50% of the test organism population within a specified time frame. Finally, the MATC is defined as the average of the LOEC and NOEC values, representing the highest acceptable concentration of a substance without causing adverse toxic effects on the test organisms.

The stimulant composition utilized in this study is defined by the NOEC value. By employing the NOEC value, the plants demonstrated the capacity to thrive until the conclusion of the observation period on day 28. This facilitates the execution of more meticulous and comprehensive observations pertaining to the plants' capacity for metal absorption. The subsequent data sets present the LOEC, NOEC, LC50, and MATC values for each plant following the incorporation of diverse stimulants, as delineated in Tables 1. and Tables 2.

Table 1. Calculation of percent mortality, LOEC, NOEC, LC50, and MATC *Cymbopogon citratus* + Manure + Red mud

Cymbopogon citratus + Manure + *Red mud*										
% Biostimulant	***% Red mud***	**d (test pollutant load) (gr)**	**n (number of test plants)**	**r (test plant mortality)**	**P1 (% survival)**	**P2 (% live mortality)**	**LOEC**	**NOEC**	**LC50**	**MATC**
0%	100%	900	9	9	0.00	100.0				
5%	95%	855	6	6	0.00	100.0	855	810	875.36	832.20
10%	90%	810	23	2	91.30	8.7				

Table 2. Calculation of percent mortality, LOEC, NOEC, LC50, and MATC *Portulaca grandiflora* + Manure + Red mud

Portulaca grandiflora + Manure + *Red mud*										
% Biostimulant	% *Red mud*	d (test pollutant load) (gr)	n (number of test plants)	r (test plant mortality)	P1 (% survival)	P2 (% live mortality)	LOEC	NOEC	LC50	MATC
0%	100%	600	153	153	0.00	100.00	570	540	611.18	554.80
5%	95%	570	151	55	63.58	36.4				
10%	90%	540	23	0	100.00	0.0				

In addition to quantitative testing, qualitative testing was also conducted.Based on observations, the addition of 10% compost to red mud resulted in plant survival until day 28, while at 0% and 5% composition, the plants had died on day 14. This finding indicates that compost not only enhances the fertility of the growing medium by supplying essential nutrients but also functions as a stimulant that promotes plant root health by supplying sustenance to soil microorganisms. These microorganisms, in turn, maintain soil health and produce nitrogen and phosphorus naturally, thereby supporting plant growth (14). Furthermore, higher compost concentrations, such as 10%, have been observed to promote accelerated plant growth, as evidenced by the enhanced survival rates and phytomining effectiveness of vanadium (V) and chromium (Cr) under these conditions (15).

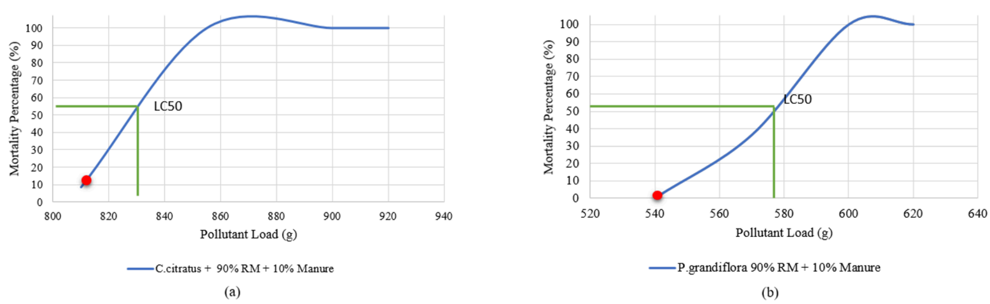


Fig. 3. Toxicity S-curve of (a) *Cymbopogon citratus* and (b) *Portulaca grandiflora*

A total of 810 grams of pollutant load in the form of red mud was utilized as a planting medium for *Cymbopogon citratus*, with the addition of 90 grams of manure stimulant. In the case of *Portulaca grandiflora*, a total of 540 grams of red mud was employed as a pollutant load in the planting media, with the addition of 60 grams of manure stimulant.

3.3 Morphology Characterisation

Prior to the commencement of phytomining, an observational study is conducted to examine the root structures of the plants in question, which are then transferred to red mud media. The following image depicts the roots of *Cymbopogon citratus* and *Portulaca grandiflora* prior to their transferral to red mud, with the objective of observing the impact of this process during phytomining.

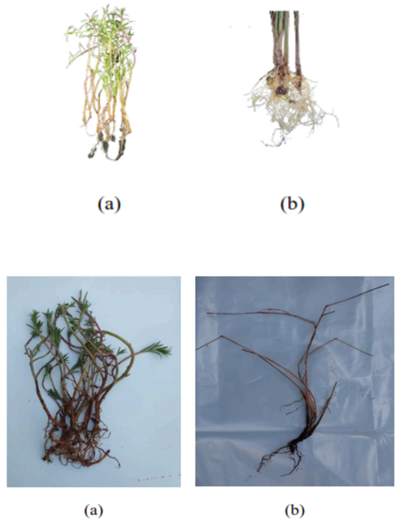


Fig. 4. Condition of (a) Root of *Portulaca grandiflora;* (b) Root of *Cymbopogon citratus* before planting for phytomining on red mud (top); Condition of (a) Root of *Portulaca grandiflora;* (b) Root of *Cymbopogon citratus* after planting for phytomining on red mud (bottom)

Figure 4. illustrates the condition of *Portulaca grandiflora* and *Cymbopogon citratus* roots prior to planting for phytomining in red mud (top) and subsequent to planting for phytomining in red mud (bottom). There are several notable changes in the plants' physical condition following the treatment and planting process on red mud. In the case of *Cymbopogon citratus*, the colour of the stem shifts to a yellowish hue, becoming dry and slightly shrunk. A similar phenomenon was observed in *Portulaca grandiflora*, where the plant stems exhibited a reduction in size when compared to their state prior to being planted in red mud.

In addition to the aforementioned physical observations, the physical characteristics of red mud were also tested. A content weight analysis of red mud with a manure stimulant was conducted to determine its effect on red mud. This is because the content weight shows the density of the media. A good weight content value to indicate healthy soil is less than 1.2 g/cm³ [16]. A higher weight content value indicates a denser growing medium. It is inadvisable to use planting media that are too dense for planting purposes. The infiltration process is prolonged, resulting in a longer period for water to leave the soil. This may lead to the deterioration of roots due to prolonged exposure to moisture. The known content weight of red mud is 1.38 g/cm³. This figure demonstrates the low grain density of red mud. However, the content weight of red mud was observed to improve following its planting with *Cymbopogon citratus* and *Portulaca grandiflora*, with the addition of 10% manure stimulant in each medium. The content weight of the red mud media with the manure mixture planted with *Cymbopogon citratus* on the 28th day changed to 1.04 gr/cm³, while the content weight of the red mud media with the manure mixture planted with *Portulaca grandiflora* changed to 0.99 gr/cm³. These findings demonstrate that the addition of manure can enhance the density of red mud, thereby providing a supportive environment for plant growth.

3.4 Phytomining

During phytomining, the pH and electrical conductivity (EC) were monitored on a regular basis to assess the metal content. The phytomining process entailed three sampling points, at which the metal content and pH and EC tests were conducted. These took place on days 0, 14, and 28.

A decline in pH was observed in each measurement taken, which may be attributed to the addition of biostimulants. As stated by [11], the incorporation of manure can result in a reduction of soil pH. The addition of acidic media to red mud with a very alkaline pH can reduce pH to a certain extent [17]. In addition to lowering pH, manure made from animal manure can also increase nutrient retention in red mud [18]. The mechanism of action of manure fertiliser from animal manure is the gradual release of nutrients, which prevents a drastic and rapid decrease in the nutrients present in red mud.

In contrast to the observed decrease in pH across all tests, the trend in electrical conductivity (EC) exhibited an increase until day 28. This phenomenon can be attributed to the presence of salt-soluble ions such as Ca++, Mg4+, Na, NH2-, SO4, etc., in the manure, which contribute to an increase in electrical conductivity (EC) within the media. A similar phenomenon was observed in a study conducted by [12], wherein the addition of manure fertilizer in the form of cow dung resulted in an increase in electrical conductivity (EC) in the soil. Furthermore, manure fertiliser contains organic acids that can elevate the pH of red mud, which is highly alkaline, thus facilitating the formation of salt and augmenting EC levels. Additionally, the enhancement of media porosity exerts an influence on the rise in EC. As documented in the National Soil Survey Handbook, elevated soil porosity is associated with elevated EC levels.

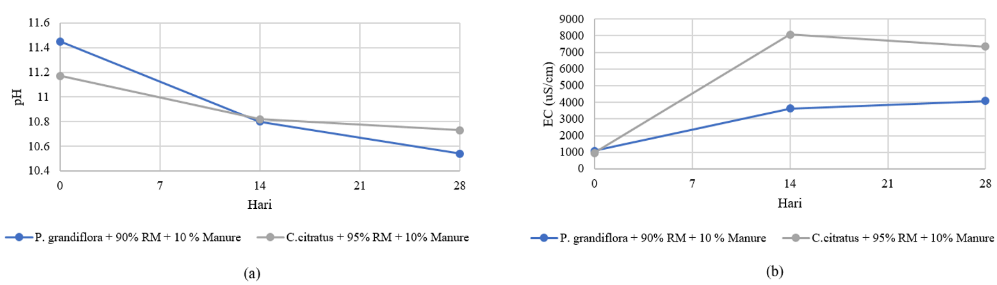


Fig. 5. Fluctuation of (a) pH and (b) EC during phytomining

3.4.1 Metal content of V and Cr

As with the pH and EC measurements, vanadium and chromium levels were assessed on days 0, 14, and 28 of phytomining. The subsequent figures illustrate the visualization of Cr and V levels in bar graphs, which facilitate the interpretation of the decreasing and increasing trends in metal levels over the course of the sampling period.

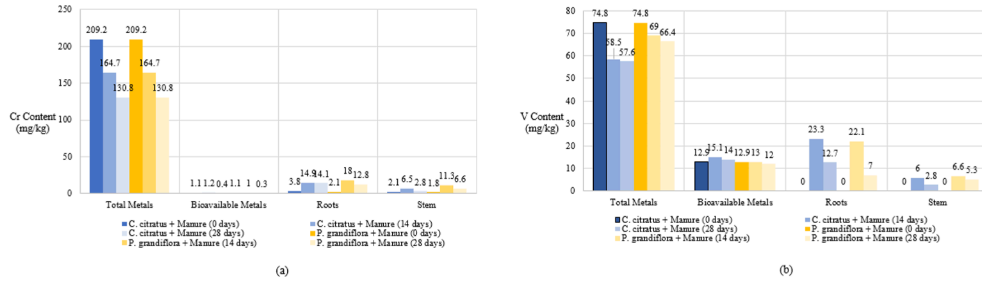


Fig. 6. The content of (a) Cr and (b) V content in *Cymbopogon citratus* and *Portulaca grandiflora*

Figure 6 illustrates the capacity of *Cymbopogon citratus* and *Portulaca grandiflora* plants to absorb heavy metal element V. The graph indicates that *Cymbopogon citratus* could absorb up to 23.3 mg/kg V in roots and 6.05 mg/kg V in stems on day 14. The highest levels of vanadium uptake were observed on day 14 in *Cymbopogon citratus*. The value declined on day 28. Conversely, *Portulaca grandiflora* plants demonstrated the capacity to take up to 28.6 mg/kg V, of which 22.1 mg/kg V was absorbed in the roots and the remaining 6.6 mg/kg V was translocated to the stem. The highest value of metal absorption was observed on day 14, with a subsequent decrease on day 28, where metal levels were recorded at 12.3 mg/kg. It is notable that a considerable amount of the metal, up to 7 mg/kg V, remained in the roots, while 5.3 mg/kg V was present in the stem.

Cymbopogon citratus demonstrated the capacity to absorb up to 14.9 mg/kg Cr in roots and 6.5 mg/kg Cr in stems on day 14. The highest Cr uptake was observed on day 14 in *Cymbopogon citratus*, although this value decreased on day 28. A similar trend was observed in *Portulaca grandiflora* plants, where the largest Cr uptake occurred in the roots on day 14 at 18 mg/kg, which then decreased to 11.3 mg/kg on day 28.

The greatest uptake of V metal was observed in *Cymbopogon citratus*, which received a manure addition treatment of 10% of the total media. The uptake was 23.3 mg/kg in the roots and 6 mg/kg in the stem. The greatest absorption of Cr metal was observed in *Portulaca grandiflora* when manure was added at a rate of 10% of the total media, with an uptake of 18 mg/kg in the roots and 11.3 mg/kg in the stem.

It can therefore be concluded that both plants demonstrated enhanced capacity for V metal absorption with the addition of 10% manure fertiliser. This is due to the fact that manure fertiliser contains significant quantities of organic acids. In the study conducted by [19], the application of 5 grams of manure fertilizer resulted in enhanced Cr metal absorption by Jatropha curcas, in comparison to plants that were not provided with manure fertilizer. This argument is also supported by [20], which demonstrates that the presence of organic acids is directly correlated with a plant's capacity to tolerate elevated metal levels in the environment. In his research, wheat secreted organic acids, including citrate and malate, to enhance its tolerance to aluminium. Organic acids are also involved in the sustainability of the ascorbate-glutathione cycle, which plays a role in forming complex bonds with metals, thereby enabling plants to withstand environmental stress [21].

3.4.2 Biocummulation Factor (BCF) and the Translocation Factor (TF)

The results of the measurements of the metal content of vanadium (V) and chromium (Cr) obtained by inductively coupled plasma optical emission spectrometry (ICP-OES) were used to calculate the values of the Biocummulation Factor (BCF) and the Translocation

Factor (TF). The values of the TF and BCF for the metals Cr and V are presented in the Table 3.

Table 3. TF and BCF values of Cr and V metal in plants.

Parameter	Metal	Reactor	Days of Observation	
			14	28
TF (mg/plant)	V	*C. citratus* + RM 90% + 10% Manure	0.26	0.22
		P. grandiflora + RM 90% + 10% Manure	0.30	0.75
	Cr	*C. citratus* + RM 90% + 10% Manure	0.44	0.20
		P. grandiflora + RM 90% + 10% Manure	0.63	0.51
BCF(mg/plant)	V	*C. citratus* + RM 90% + 10% Manure	1.81	0.99
		P. grandiflora + RM 90% + 10% Manure	1.71	0.55
	Cr	*C. citratus* + RM 90% + 10% Manure	14.01	13.3
		P. grandiflora + RM 90% + 10% Manure	36.04	25.66

The data presented in Table 3. allows for the formulation of conclusions regarding the ability of plants to absorb V and Cr metals in the presence of stimulants. The results demonstrated that the highest absorption of V and Cr metals was achieved with *Cymbopogon citratus* when manure stimulants were added at a ratio of 10% to the total media. It is established that *Cymbopogon citratus* has an MEA value of 0.26 mg/plant for V and 0.19 for Cr. With regard to Cr, the maximum absorption value was attained in the phytomining process over a period of 14 days.

3.5 Conclussion

This research employs the use of *Cybopogon citratus* and *Portulaca grandiflora* plants for the extraction of vanadium and chromium metals from red mud, with the addition of manure fertilizer as a stimulant. *Cymbopogon citratus* showed the highest absorption of vanadium, with up to 23.3 mg/kg in the roots. *Portulaca grandiflora* exhibited the highest absorption of chromium, with concentrations reaching 18 mg/kg in the roots. TF and BCF analysis show about the accumulation of metals in plants. it should be seen that TF has an average value of less than 1 with the highest value is in *Portulaca grandiflora* plants for vanadium metal of 0.75, meaning that metals will accumulate only in the roots. Then the relatively large BCF up to 36.04 for Cr metal in *Portulaca grandiflora* plants indicates the ability of metal accumulation from the environment into plants. The use of these plants for phytomining offers an environmentally friendly alternative for remediating heavy metal-contaminated sites, reducing the ecological risks associated with red mud.

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