Preliminary Study on Potential of EAF Slag as Nutrients Source for Mangrove Seedling

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Abstract. Electric Arc Furnace (EAF) slag generated from steel making process mainly consist of calcium oxide (CaO), iron oxide (FeO), silicon oxide (SiO₂), manganese oxide (MnO), aluminium oxide (Al₂O₃) and magnesium oxide (MgO) in different phases. Since the elements are matching some of the nutrients or micro-nutrients that are needed in plant growth, this study was carried out with the purpose of finding the potential of EAF Slag as nutrients source for mangrove seedling in nursery centre. EAF slag taken from steel making plant during normal production process was crushed and analysed with XRF to obtain chemical composition result and XRD for phase analysis. ICP-OES elemental test was done on leachate from kinetic leaching experiment to assess the leaching trend for each elements form EAF slag in distilled water. Result obtained shows Ca and Si are the major elements that leached from EAF slag with uptrend line, and achieved about 25 mg/l for Ca and 7.5 mg/l for Si after 10 days in distilled water with L/S ratio as main affecting factor. Fe and Mn leaching will be enhanced by stirring at highest speed of 700 rpm. Both elements show uptrend with highest leaching at 0.27 mg/l for Fe and 0.14 mg/l for Mn at day 10, and this shows good potential of EAF slag as slow release element. Mg as an important element in chlorophyll shows uptrend leaching to about 1.5 mg/l at day 10, with L/S ratio as main influential factor. Potassium (K) and sodium (Na) leaching fluctuated below 0.50 mg/l for K and below 0.08 mg/l for Na. Al is the only element that achieved highest level in between day 3 to 7, and then drop gradually to day 10, at about 1.0 mg/l for sample with 700 rpm stirring speed. The results showed good potential for EAF slag to be used as slow release nutrients source for mangrove seedling. Further studies are currently underway to evaluate the effect of EAF slag in altering pH of the soil, as well as efficiency of EAF slag as fertilizer for mangrove plant by observing the growth rate of seedling planted in mangrove nursery site.

1. Introduction

The Tsunami of 26 December 2004 had caused at least 167,000 of lives and 500,000 of homes in Aceh, Indonesia. Besides, it swept away 800 km of mangrove forest along the coastal of the province of Nanggroe Aceh Darussalam [1]. Since then, mangrove forest protection and restoration become one of the major activities in building up protection to community along the coastal area, especially in east
Asia. Thousands of people and millions of dollars were involved in mangrove forest planting and restoration in tropical and subtropical coastline.

1.1 Mangrove in Malaysia. There are 641,886 ha of mangrove forests in Malaysia, which is less than 2% of the total land area in Malaysia, at about 329,758 km². 57% of the mangrove forests are found in Sabah and 26% in Sarawak, with remaining 17% in Peninsular Malaysia, which is 106,554 ha. From this, 69% (441,092 ha) of the mangrove forests have been gazetted as forest reserves [2].

The oldest silvicultural systems for systematic mangrove forests management were developed in Malaysia since 1902 in Matang Mangrove Forest Reserve (MMFR), Peninsular Malaysia, which was still considered as the best managed mangrove forest in the world.

But, forest conversion to agriculture have intensified beginning in the early 1970s. Over a period of 22 years from 1970 to 1992, natural forest in Malaysia was reduced by 19.3% due to conversion of forest land to agricultural land especially for agricultural crops, oil palm and rubber. Lowland dipterocarp forests were affected the most. Peat swamp forests, freshwater swamp forest and mangrove forests were affected as well [3].

There are a lot of mangrove forest related activities being promoted in order to create awareness to people, especially mangrove planting activities. Mangrove seeds were collected and grew in a plastic bag filled with muddy soil at nursery center. After about 5 to 6 months, the seedlings were adopted by participants and were planted at mangrove forest area. But, not all planted seedling survived after a year, which may due to damage by animal in the forest, abnormal dry season, or unhealthy seedling.

1.2 EAF Slag. EAF slag was generated from steel making during refining process in electric arc furnace. The slag waste was unavoidable, in fact it is good for the process in reducing energy and refractory protection. The amount of generation depends on the scrap quality and process efficiency. It is about 8 to 15% of the total raw material that is being charged into the furnace. This means that in a steel mill with one-million-ton capacity, the mill will generate about 100 thousand ton of slag yearly. Currently, there is recycling plant to handle all the slag. The slag will be treated and used to replace aggregate and sand for concrete, road base, and brick making. However, the use of such aggregate is rather limited and could not successfully re-use all of the generated slag. Instead of just recycled the EAF slag as normal waste, the slag which is rich in Ca, Si, Fe, Al, Mn and Mg has created and attracted the interest of researcher to create value for EAF slag in new or advance applications.

Therefore, this study was initiated to find out the potential of re-using EAF slag as nutrients source for seedling growth of mangrove plant.

2. Experimental study

2.1 EAF slag sample. EAF slag sample was taken from electric arc furnace slag pit, in dry form during normal steel making production. It was analyzed by SPECTRO XEPOS XRF to obtain chemical composition; inspected under EVO MA 10 Zeiss SEM and analyzed with INCA Penta FETx3 EDX to obtain chemical composition.

The raw slag sample was ground by disc mill to size 0.15-0.25, 0.25-0.5 and 0.5-1.0mm, and then used in kinetic leaching test for 10 days with liquid to solid (L/S) ratio of 20:1, 60:1 and 100:1 in distilled water, with stirring speed at 0, 350 and 700 rpm by Simarec Magnetic stirrer. The leachates were analyzed by Induced Coupled Plasma - Optical Emission Spectrometry (ICP-OES), PerkinElmer Optima 7300DV, to determine the quantity of Ca, Si, Fe, Al, Mn, Mg, K and Na.

2.2 Rhizophora mangrove leaves sample. Mangrove leaves were taken from mangrove forest at Kampung Batas Ban, Nibong Tebal, P. Pinang, Malaysia. 10 fresh leaves were sampled from each of the 5 mangrove trees. The fresh leaves were dried in an oven at 105°C for 24 hours and analyzed by SPECTRO XEPOS XRF to determine the nutrients element content.
3. Results and discussion

Results of all the experiment were obtained and compiled for subsequent discussion.

3.1 Chemical composition, physical structure and kinetic leaching characteristic of EAF slag

Table 1 shows the EAF slag analysis result by XRF. Result shows that the EAF slag has Ca as the highest element and followed by Fe, Si, Mn, Al and Mg.

Table 1. XRF analysis result of EAF slag (weight %).

| Sample   | Ca   | Fe   | Si   | Mn   | Al   | Mg   |
|----------|------|------|------|------|------|------|
| EAF Slag | 29.8 | 20.2 | 17.3 | 8.17 | 6.13 | 5.61 |

Based on the result obtained from SEM-EDX in Figure 1, the EAF slag appeared in irregular shape and based on the EDX analysis, consisted mainly of iron oxide and calcium silicate.

Figure 1: SEM-EDX inspection result of physical structure and element content in EAF slag

Result from Figure 2 shows the 10 days kinetic leaching for each test elements. Ca is the main element that leached out from slag in kinetic leaching test. It achieved about 25 mg/l after 10 days. Si is the second most leached element at about 8 mg/l followed with Mg at about 1.5 mg/l. Three elements show the highest leaching with L/S ratio of 20:1, without significantly affected by stirring speed. Leaching of Fe and Mn at stirring speed 700 rpm showed uptrend line. At day 10 of the experiment, Fe achieved highest at 0.27 mg/l and Mn at 0.14 mg/l. Low leaching concentration was detected for K and Na. Leaching concentration of K fluctuated below 0.5 mg/l and Na fluctuated below 0.08 mg/l. Al is the only element that achieved highest level in between day 3 to 7, and then drop gradually to day 10, at about 1.0 mg/l for sample with 700 rpm stirring speed.
3.2 Nutrients element concentration in Rhizophora mangrove leaves

Figure 3 shows the nutrients element of mangrove in a kg of dry leave weight.

Figure 3: XRF analysis result of Rhizophora mangrove leaves (mmol/kg of dry Weight).
3.2.1 Method of analysis for nutrient elements concentration. In the study of nutrients in sediment and mangrove leaves by Bernini et al. [4], nutrient content was determined using methods described by Sarruge & Haag (1974) and Silva (1981), which is the use of nitric perchloric acid digestion to extract Ca, Cu, Fe, K, Mg, Mn, P, S and Zn. The determination of total P was done by colorimetry (725nm), S was determined by gravimetric determination based on the precipitation of sulphur by barium chloride, in the form of barium sulphate, and other elements by conventional atomic absorption spectrophotometry.

Most of the plant nutrient elements were analysed by Induced Coupled Plasma - Optical Emission Spectrometry (ICP-OES) [5] or Atomic Absorption Spectrophotometry (AAS) [4] [6]. But XRF was also being used in research work to determine the nutrients element in plant [7] [8]. Compared with conventional ICP and AAS methods, XRF has the advantages of simple sample preparation, sample in small quantity, less time spend for analysis test and less cost involved. The studies suggested that XRF technique could be an alternative analysis method for nutrient analysis [7].

Even though XRF has the limitation of unable to analyze low atomic number elements like carbon (C), hydrogen (H), oxygen (O) and nitrogen (N), but in this study, main study elements are not C, H, O and N. Thus, with the facility and reference that available, SPECTRO XEPOS XRF was used to analyze the elements in mangrove leaves.

3.2.2 Nutrients element in mangrove leaves. In mangrove leaves, nutrients followed the sequence of N> Ca> K> Mg> S> P> Fe> Mn> Zn> Cu and there was significant difference between mangrove species and sites of the studies [4].

Table 2 shows the comparison of leave nutrients element in this study with 2 results from Khafaji et al. [6] and Medina et al. [5]. The concentration results are different from each other. It may be due to different species and mangrove forest that the leaves were sampled as highlighted by Bernini et al. [4]. But the sequence of nutrients concentration was similar in all the study as presented in table 2.

| Element          | Rhizophora apiculata Result in this study | Rhizophora mucronata (Khafaji et al. [6]) | Rhizophora mangle (Medina et al. [5]) |
|------------------|-----------------------------------------|------------------------------------------|----------------------------------------|
| Sodium (Na)      | % mmol/kg                                | % mmol/kg*                               | mmol/kg old leaf **                    |
| Chlorine (Cl)    | 4.06 1766                                | 1.81 787                                 | ~ 500                                  |
| Calcium (Ca)     | 3.35 945                                 | -                                        | -                                      |
| Magnesium (Mg)   | 1.01 416                                 | 0.62 255                                 | ~ 190                                  |
| Potassium (K)    | 1.12 285                                 | 0.69 176                                 | ~ 120                                  |
| Sulphur(S)       | 0.552 172                                | -                                        | -                                      |
| Silicon (Si)     | 0.249 89                                 | -                                        | -                                      |
| Phosphorus (P)   | 0.231 75                                 | 0.14 45                                 | -                                      |
| Aluminium (Al)   | 0.177 65                                 | -                                        | -                                      |
| Manganese (Mn)   | 0.163 30                                 | 0.0216 4                               | ~ 10                                   |
| Iron (Fe)        | 0.119 21                                 | 0.0109 2                              | ~ 1.5                                  |
| Titanium (Ti)    | 0.0132 2.76                              | -                                        | -                                      |
| Vanadium (V)     | 0.0061 1.19                              | -                                        | -                                      |
| Chromium (Cr)    | 0.0076 1.46                              | -                                        | -                                      |
| Zinc (Zn)        | 0.0017 0.25                              | 0.0034 0.52                             | -                                      |
| Copper (Cu)      | 0.0009 0.15                              | 0.00054 0.08                           | -                                      |
| Leaf water g/g dry mass | 2.27 -              | -                                        | 2-2.3                                  |

Remark: * Calculated from % result. **Figure estimated from graph (Medina et al. 2015)

3.2.3 Micronutrients. Micronutrients such as molybdenum (Mo), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na) and copper (Cu) are required in very small quantity for synthesizing chlorophyll and some enzymes. These micronutrients are important for metabolic and physiological
process. Deficiency of these micronutrients may severely affect the efficiency of photosynthesis, carbon balance, and rate of water use in plants [9]. In the study of mangroves’ response to dissolved iron supply rate by Alongi [9], all experimental results showed that mangrove growth rate was enhanced by increasing iron supply. Maximum grow rate of Rhizophora apiculate was at 50-60 mmol Fe per meter square area per day, which is about 50% higher than control sample with 0 supply rate. In another study by Almahasheer et al. [10], result showed that the iron addition consistently led to a fast growth rate in mangrove seedling. The concentration of metallic elements with relative leaf age was presented with one of the conclusion concluded that Mn and Fe concentration were several times larger in Rhizophora mangle at all leaf stages compared with other type of mangrove, Laguncularia racemasa [5]. This shows that the Rhizophora mangle accumulated Mn and Fe more than other species.

In this work, it is observed that Ca and Si are the main leached elements from EAF slag. Ca is important in plant to prevent plant from disorder which may cause curling of leaves, stunt plant growth and death of root tips. Si on the hand, may strengthen the plant cell and prevent invading by bacteria or insect. Even though Fe and Mn which are important for plant growth, leached at low level from EAF slag, but the requirement is in minute quantity by plant. On top of that, it was observed that the leaching of Fe and Mn showed uptrend over time, and this provides the opportunity of EAF slag being used as slow release nutrients source for mangrove seedling.

4. Conclusion

At the end of current studies, it could be concluded that main elements in EAF slag, which are Ca, Fe, Si, Mn, Al, and Mg, are matching the main nutrient (>1% dry weight) of Ca and Mg; minor nutrient (0.1 – 1.0%) of Si and Al; and the micronutrient (in hundreds ppm) of Fe and Mn in mangrove leaves. High leaching rate of Ca, Si and Mg from EAF slag will improve nutrients supply to mangrove soil. Even though EAF slag shows low leaching rate of Fe and Mn, which are important for plant growth rate, but the leaching rate is in uptrend over time, creating a great potential and opportunities of EAF slag to be used as slow release nutrients source to enhance mangrove seedling growth.

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