Study of the distribution of lead (Pb) on mangrove roots (*Rhizophora mucronata*) and the utilization of mangrove roots as solid fuel

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Abstract. Industrial activities can produce valuable products as well as produce waste that can cause disturb and endanger survival of the living things. This research discusses distribution of lead (Pb) concentrations in *Rhizophora mucronata* mangrove roots which was studied through diffusion equation model and utilizes the *Rhizophora mucronata* mangrove roots as an alternative fuel. The production and testing of charcoal in this study used a simple household scale method by varying time of coking and testing of the gases resulting from charcoal containing harmful emission gases by the test method for survival experiment on insects. The result of this research is he finite difference method used in this study can poorly represent the process of lead absorption by mangrove roots as measured by a relatively high error. The lead concentration was distributed downwardly from root bark to center of the root and difference in distribution of lead concentration in each layer decreased from the first day to the thirtieth day. Solid fuel from *Rhizophora mucronata* mangrove roots according to or meet the standards of SNI 01-1682-1989, namely yield test value of 37.48%, moisture content test of 3.46%, test for the content of the volatile substance 25.87%, ash content test of 1.79%.

1. Introduction

The development of industry in Indonesia has various impacts on society and the environment in particular. A reality that must be faced due to the progress and existence of the industry in addition to having positive and negative impacts. Many industrial activities in the production process that produce valuable products also produce waste that can cause environmental pollution if not managed according to procedures properly. One type of waste that is mostly generated from industrial activities is liquid waste other than solid waste. The government, especially the Ministry of the Environment, seeks to reduce the impact of industrial waste by determining the standard requirements or quality standards for industrial area wastewater. These standards are contained in the Minister of Environment Regulation No. 3 of 2010, one of the important criteria in the quality standard of industrial processed water is the content of heavy metals.

Industrial activities can be a contributor to heavy metals in waters that empty into the sea, which can disrupt and endanger the survival of the living things in it. Heavy metals in wastewater generally can be treated physico-chemically, such as evaporation, adsorption, ion exchange, electrochemical processes, and membrane technology. However, it is undeniable that heavy metals are still scattered in the environment above the predetermined quality standards. According to Mac Farlane [1], the most metal pollutants released by industry are Cu, Pb, and Zn. Meanwhile, lead is a major pollutant in the environment and a major source of pollution because it has a wide distribution/distribution. Furthermore, mangroves can function as a barrier to the spread of heavy metals into aquatic
ecosystems. This means that mangroves can be used as phytoremediators in the phytoremediation process.

Phytoremediation is the process of cleaning pollution and contaminants in the environment using plant media. Mangroves of the *Rhizophora mucronata* species are able to accumulate lead (Pb) heavy metal [2]. The absorption of dissolved heavy metals from both sediment and sea water is carried out by the roots. Plant roots in the soil can play an important role in reducing metal content through filtration, adsorption and ion exchange. Root cells can absorb solutions containing lead by diffusion process if there is a difference in concentration. Therefore, the distribution of lead (Pb) in mangrove roots can be represented by the diffusion equation. One method that can be used to determine the solution numerically is the finite difference method. The finite difference method brings the domain of partial differential equations into the computational domain in the form of a grid so that the distribution of lead absorption can be determined [3]. For this reason, knowing the distribution of lead (Pb) concentrations in mangrove roots (*Rhizophora mucronata*) needs to be known as an environmental evaluation medium to control industrial waste disposal activities so that water pollution due to industrial waste can be overcome.

*Rhizophora mucronata* is a type of mangrove that is easy to grow in mangrove forests. Based on a survey by the Ministry of Forestry in 2010 the area of mangrove forests in Indonesia is around 3.7 million hectares and spread on the island of Java is only about 35 thousand hectares. Mangrove plants of the *Rhizophora mucronata* type provide many benefits including being able to be used as quality mangrove charcoal with a high calorific value with a large calorific value of 3,088 cal/g. The use of alternative energy is very much needed to anticipate the fossil fuel crisis. While the need for fuel for human life is very important and day by day the use of fuel is increasing in balance with the increase in population, while the amount of fossil fuels is dwindling. Indonesia's oil reserves are at position 28 or 0.2% of the world's oil reserves of 3.7 billion barrels. Oil reserves are predicted to run out over the next 50 years, while natural gas will run out in the next 50-100 years [4]. Therefore, in addition to being a phytoremediator, mangroves (*Rhizophora mucronata*) can be used as an alternative to solid fuels.

2. Materials and Methods

2.1 Finite Difference Method

One of the popular methods is the Finite Difference and Finite Element method. The finite difference method can produce a form of simultaneous linear equation [5]. There are two types of boundary conditions problems, namely if they are in the boundary area or fixed boundary conditions, then this constraint is called the Dirichlet boundary condition [6], as:

\[ U(x,y) = g(x,y) \]  

Meanwhile, if the boundary conditions are in the form of a derivation, it is called the Neumann boundary condition as:

\[ \frac{dU(x,y)}{dn} = 0 \]

The solution using the finite difference method can be explained by considering an area which is the result of a partial differential equation which has one dependent variable u and two independent variables x and t. Each differential equation that applies to the area expresses the state of a point or gap that is quite small in the area. The FTCS (Forward Time Center Space) method is often referred to as the explicit method for the diffusion equation. This method is applied to ut with an accuracy of 0 (∆x^2) and the Backward Difference method is applied to uxx with an accuracy of 0 (∆x^2) with ∆x = h and ∆t = k. [2].

2.2 Error

Science is very broad and much is done to obtain quantitative and qualitative data. Quantitative data is obtained from calculations in a study or experiment, because the calculations are carried out in a study, the error value is obtained. Error is a term used to determine the numerical difference between the calculated value and the actual value [7], error is the difference between the exact and approximate value [8]. If xi is the value of an approximation for the exact value of x, then the error is as follows:
Absolute error is the absolute value of an error, while relative error is the ratio between the (absolute) error and the exact value \[8\]. To obtain the value of \(e\) or the average with the best estimates, the average value of \(e\) is calculated as follows \[9\]:

\[
x = \frac{1}{N} (x_1 + x_2 + \cdots + x_N) = \frac{1}{N} \sum_{i=1}^{N} x_i
\]

2.3 Charcoal Carbonization

Carbonization is defined as a process of breaking down organic matter into charcoal in the absence of air. Carbonization or pyrolysis is a chemical decomposition process using heating in the absence of oxygen. The process of writing or carbonization is divided into four stages \[10\], namely:

1. The water evaporation stage occurs at a temperature of 100 - 105ºC.
2. Decomposition of hemicellulose and cellulose at a temperature of 200 - 240ºC into a pyrolignite solution.
3. The process of depolymerization and breaking of C-O and C-C bonds at a temperature of 240 - 400ºC.
4. The stage of formation of the aromatic layer occurs at a temperature of more than 400ºC and the lignin still continues to decompose until a temperature of 500ºC, while at a temperature of more than 600ºC, the surface area of the charcoal enlarges. Furthermore, the charcoal can be purified or made into activated charcoal at a temperature of 500 - 1,000ºC.

The duration of the cooking process is determined by the volume of organic matter, the partial size of the material, the density of the material, the degree of dryness of the material, the amount of oxygen entering and the smoke coming out of the combustion chamber. In summary, carbonization process can be shown in Figure 1 \[11\].

![Figure 1. Complete Carbonization Process Including Its Products \[11\]](image)

In Indonesia, wood charcoal briquettes for wood raw materials, hard skin and coconut shells already have SNI standards with SNI number 01-1682-1989 with the quality requirements shown in the Table 1.

| Parameter                  | Wood Charcoal Quality Standard |
|----------------------------|--------------------------------|
| Water Content              | 6%                             |
| Ash Level                  | 4%                             |
| Evaporative Substance Level| 30%                            |
| Heat Value                 | 5000 Cal/g                     |
2.4 Study of The Distribution of Heavy Metal Lead (Pb)

This chapter describes the methods and stages of research on the distribution of lead (Pb) heavy metal using MATLAB R2013a and the manufacture of solid fuels from phytoremediation *Rhizophora mucronata*.

The tools used in the research are to study the distribution of heavy metal lead (Pb) using MATLAB R2013a software and to manufacture solid fuels using ovens, saws, analytical balances, cooking containers, furnaces and other supporting tools. The materials used in the study were the roots of *Rhizophora mucronata*, burning barrels, rice bran, matches, fuel.

The variables in this study consisted of two stages. Phase 1 is a study of the distribution of heavy metal lead (Pb) using phytoremediation method using plants *Rhizophora mucronata*, while phase 2 is the manufacture of solid fuel from *Rhizophora mucronata* as a result of phytoremediation. The variables in this phase 1 research are divided into 2, namely independent variables and fixed variables. The fixed variables in this study were the temperature at the time of acclimation 28-30˚C, root diameter: 0.1 dm, diffusion coefficient of lead = $1.5120 \times 10^{-7}$ dm$^2$. The independent variables in this study were obtained from the results of journals or previous studies, namely the initial value of lead (Pb) concentration in the roots due to the acclimation process, time, lead metal content (Pb) from previous studies. While the variables in phase 2 research are divided into 2, namely independent variables and fixed variables. The fixed variable in this study is the burning time, while the independent variable in this study is the mass of the raw material for making charcoal, namely the mangrove roots of *Rhizophora mucronata*.

2.5 Procedures

The research procedure in this study there are 2 stages. Stage 1 is the process of absorption of heavy metals from marine waters using the phytoremediation method using *Rhizophora mucronata* plants, while stage 2 is the manufacture of solid fuels from phytoremediation *Rhizophora mucronata*. The research procedure in Phase 1 used research methods based on a numerical approach. The initial stage of this research is a literature study to find references that are appropriate to the research subject. The next step is data collection. Then identify the problem, this problem identification is done to find out the existing problems so that research assumptions can be determined. The next step is to build a modified model of the diffusion equation of the lead (Pb) flow model in mangrove roots (*Rhizophora mucronata*). Then apply the explicit finite difference scheme (FTCS) to the lead (Pb) flow model in mangrove roots (*Rhizophora mucronata*).

The next step is to determine the initial value and boundary conditions based on the data that has been collected. Then determine and perform numerical calculations manually which is then simulated and interpreted using the MATLAB R2013a program. While the research procedure in stage 2 is through the manufacturing steps, starting with taking the roots of *Rhizophora mucronata* from phytoremediation on the coast of Gresik. The roots were taken because of the age factor of the roots of *Rhizophora mucronata* which had an age of about 8 months, because at that age the absorption of heavy metals from the roots began to decrease, then cut the roots of *Rhizophora mucronata* for 15cm, drying the roots of *Rhizophora mucronata* with the help of sunlight, then the writing was done, then continued with the characterization test.

The characterization test in this study was divided into 4, namely water content test, calculating yield, fixed carbon, and volatile matter content test. The water content test serves to determine the water content in the charcoal, calculating the yield serves to determine the amount of charcoal produced after the carbonization or cooking process. Ash content test was carried out to determine the metal oxide content in charcoal. The volatile substance content test is carried out to determine the content of compounds that have not evaporated.

3. Results and Discussion

Tables or figures are presented in a format The general form of the diffusion equation used in this study is the following equation:

$$ut = kuxx$$

(5)
The value of \( u \) represents the lead concentration at location, time, and represents the diffusion coefficient. To maintain the value of the concentration of lead that is diffused in the mangrove roots continues to increase due to absorption, equation (5) is modified to:

\[
\frac{du}{dt} = kuxx + (x) \tag{6}
\]

\( x \) is a function that expresses the external factor that represents lead absorption by mangrove roots. By using the FTCS scheme, the variable concentration of lead, \( x \), and its derivatives twice in space and time is as follows:

\[
\frac{u(x,j)}{\partial t} = \frac{1}{\Delta t} \left( u_{j}^{n+1} + u_{j+1}^{n} + 2u_{j}^{n} + u_{j-1}^{n} \right) \tag{7}
\]

\[
\frac{u(x,j)}{\partial x^2} = \frac{1}{\Delta x^2} \left( u_{j+1}^{n} - 2u_{j}^{n} + u_{j-1}^{n} \right) \tag{8}
\]

By applying equations 7 and 8 to equation 5 and rearranging the corresponding terms, we get as follows:

\[
u_{j}^{n+1} = u_{j}^{n+1} + ku_{j}^{n} + (x) \tag{9}
\]

Where \( u_{j} = u(x_{j}), j = 1 ... N \). The value of \( N \) is the number of grids. Equation (5) can be written as:

\[
u_{j}^{n+1} = s(u_{j+1}^{n} + u_{j-1}^{n}) + (1 - 2s) u_{j}^{n} \tag{10}
\]

\[
S = K \frac{\Delta t}{\Delta x^2} \tag{11}
\]

The initial value used in this study was the concentration of lead in the bark of the mangrove roots in the acclimation process of 1.82 ppm. Then the assumption of the concentration value in the media on the left and right is the same, which is half the domain. So, the calculation is only half the domain. Then the left boundary condition used is the concentration in the media and the right boundary condition used is the midpoint of the root, which is presented as follows:

\[
ux (x = \frac{L}{2}, t) = 0 \tag{12}
\]

With an \( x \) value of 0.0167, the number of half-domain grids (\( N \)) = 3, and \( t = 10 \). And the diffusion coefficient used is \( 1.512 \times 10^{-7} \text{dm}^2 \). Then calculated the S value of 0.00542. So, the equation used in the study is equation 10 which is substituted with equation 6 as follows:

\[
u_{j}^{n+1} = S(u_{j+1}^{n} + u_{j-1}^{n}) + (1 - 2s) u_{j}^{n} + f(x_{j}) \tag{13}
\]

Then from these equations, numerical calculations are carried out through MATLAB R2013. The results of numerical calculations through MATLAB are obtained as given in Table 2.

| Table 2. Calculation Results Using MATLAB R2013 |
| J = 0 | J = 1 | J = 2 | J = 3 |
|-------|-------|-------|-------|
| X1 = 0 | X2 = 0.0167 | X3 = 0.0334 | X4 = 0.05 |
| n = 0 | t = 0 | 10 | 0.91 | 0.91 | 0.91 |
| n = 1 | t = 10 | 9.96 | 1.0626 | 1.0191 | 1.0188 |
| n = 2 | t = 20 | 8.465 | 1.0425 | 1.0023 | 1.0020 |
| n = 3 | t = 30 | 7.5405 | 1.0209 | 0.9855 | 0.9853 |
Table 3 is the result of the calculation of the error used to measure the accuracy of a numerical method used in this study:

**Table 3. Daily Error Calculation Results**

| Day | Concentration (ppm) | Numerical Calculation Results (ppm) | Absolute Error | Relative Error |
|-----|---------------------|-------------------------------------|----------------|---------------|
| 10  | 0.475               | 3.10520                             | 2.6302         | 0.8470        |
| 20  | 2.0105              | 3.04680                             | 1.0363         | 0.3401        |
| 30  | 2.935               | 2.99170                             | 0.0567         | 0.0186        |

Error analysis in this study was conducted because error analysis is very important to measure the accuracy of a numerical method. The smaller the resulting error, the more accurate the numerical solution obtained. From the numerical solution obtained in this study, it shows that the accumulation of lead concentration in mangrove roots is increasing every day. The average error is 0.40196. So, the error value indicates the inaccuracy of the numerical method of the research data used. Figure 2 shows Distribution of Lead (Pb) on Mangrove Roots *Rhizophora mucronata* Using MATLAB R2013.

![Distribution of Lead (Pb) on Mangrove Roots *Rhizophora mucronata* Using MATLAB R2013](image)

The x axis on the graph represents the value of each location point on the mangrove roots and the Y axis shows the value of the lead concentration in the roots. From the graph, it can be seen that the lead concentration was distributed decreasingly from the root bark to the center of the root and the difference in the distribution of lead concentration in each layer from the root bark to the center of the root was getting smaller from the first day to the thirty days. This is in line with the diffusion phenomenon, namely the transfer of lead levels from high concentrations to low concentrations, in the media towards the center of the roots.

In the process of making solid fuel from the mangrove roots of *Rhizophora mucronata* after the composing process, the next step is to conduct a characterization test of the charcoal or solid fuel from the mangrove roots of *Rhizophora mucronata* resulting from the writing and the results obtained in this study are given in Table 4.
Table 4. Yield Test Results, Moisture Content, Volatile Matter Content, Ash Content, Solid Fuel Manufacture

| Parameter                      | Mangrove Root Charcoal | SNI 01-1682-1989 |
|--------------------------------|------------------------|------------------|
| Yield                          | 37.48%                 | -                |
| Water Content                  | 3.46%                  | 6%               |
| Evaporative Substance Level    | 25.87%                 | 30%              |
| Ash Level                      | 1.79%                  | 4%               |

From table 4 it can be concluded that the higher the % yield, the better the quality of charcoal. The calculation of the % yield value in this study was carried out to determine the amount of charcoal produced after the cooking or carbonization process. The longer the burning time, the higher the percentage yield, the higher the carbonization temperature, the lower the percentage yield. In addition, the yield value can be influenced by the specific gravity of the material. The % yield obtained in this study was 37.475%. Materials with higher specific gravity are denser, so they are more resistant to being degraded by heat of cooking and cause high yield values [12]. The stages that can affect the yield of charcoal are the combustion process in the drum furnace. The heat generated comes from outside the system and the combustion does not come into direct contact with the raw materials in the drum but is in the form of heating from the outside so that the temperature inside the drum becomes more stable and evenly distributed until it becomes charcoal [13-15].

After that, the water content test is calculated. Table 3 shows that the average obtained is 3.46%, this is in accordance with SNI 01-1682-1989 with a water content limit in charcoal of 6% if the water content exceeds the SNI limit, the charcoal ignition (ignition factor) will take longer because the water content is still quite a lot. In addition, the higher the percentage of water content contained in the sample, it will affect the calorific value obtained. Then the volatile matter test results in a volatile substance level of 25.87% so that the level is in accordance with SNI, which is 30%. The higher the percentage of volatile substances has lower ignition temperature [16]. Meanwhile, the lower the percentage of volatile substances, the slower the ignition process will be, besides the results of the carbon content and calorific value obtained will be lower if the volatile substance content is high [17]. The low volatile matter content is also influenced by the temperature of the cooking process. When the temperature used during the carbonization process is high, many levels have evaporated such as CO, CO₂, H₂, H₂O and CH₄ so that the percentage value produced is low [20]. Then the ash content test obtained the ash content in the charcoal sample of 1.79%. The ash content obtained was in accordance with SNI, namely 4%. The lower the ash content produced, the better the charcoal produced, if the ash content exceeds the SNI limit, the charcoal has a small surface area so that it can slow down the combustion process or ignition. In addition, if the percentage of ash content produced is high, it will cause a low calorific value.

4. Conclusion
The finite difference method used in this study can represent the process of absorption of lead by mangrove roots poorly as measured by a relatively high error. The lead concentration was distributed decreasingly from the root bark to the center of the root and the difference in the distribution of lead concentration in each layer from the root bark to the center of the root was getting smaller from the first day to the thirty days. Charcoal or solid fuel from mangrove roots Rhizophora mucronata conforms to or meets the standards of SNI 01-1682-1989, namely yield test value of 37.48%, water content test of 3.46%, volatile matter test 25.87%, test ash content of 1.79%.

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