Use of stearyl amine as a collector of heavy metal from boiler ash in pulp and paper industry

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Abstract. Beside contains chemical elements that can be utilized for fertilizer, boiler ash as one of mill waste from pulp and paper industry also contains transition metals in the form of heavy metal such as Boron (B), Chrome (Cr), Cobalt (Co), Cupprum (Cu) and Cadmium (Cd). These heavy metals may cause some environment issues if use directly as their concentrations is higher than the threshold level. It is become a current and continuous trend in industry to implement green technology in order to reduce the impact of mill waste into environment by reducing, extracting and removal of these heavy metals. A system extraction by using stearyl amine as a collector for heavy metal combined with organic solvent such as ethanol and n-hexane as media was proceeded to reduce some elements from boiler ash. Stearyl amine at 15 g worked more powerful in n-hexane compared to ethanol, that after 4 hours processes the elements were reduced at 40%, 43%, 55%, 67% and 76% for B, Cr, Co, Cu and Cd respectively.

1. Introduction

In pulp and paper industry, landfills is one of the common method used as a current final destination for solid waste management. Landfills are often the most cost-efficient method to dispose of solid waste; however landfills still have the potential to cause some of environment issues because solid waste may have high organic content, pathogens, ash and heavy metal that may cause contamination of soil, groundwater or aquifers [1]. There are some types of pulp and paper solid mill waste, these include boiler ash, dregs & grits, lime mud, screen reject and sludge [2]. Both boiler ash and dregs are the most abundance types of solid mill waste produced, where the proportion are 77% and 20% respectively [2]. Considering that the pulp and paper industry generates significant solid mill waste that require large open space, the implementation of legislation toward more environmental friendly policy such as government policy in PP no. 101 in 2014 [3] about toxic and hazardous waste management and increased of taxes; landfill may quickly being eliminated as a final destination for solid waste management. In response to the requirement and challenges, the pulp and paper industries need to investigate and find better solid mill waste management instead of landfills.

Some studies have been conducted to examine the feasibility of using these solid waste in construction and concrete manufacture such as in brick production, cement mixture materials and road making [4, 5]. Several other studies are looking into the feasibility of using boiler ash and sludge for land application. Considering the highest proportion of solid mill waste is boiler ash, we focus our current research on disposal of boiler ash as land application. Beside it has the ability to increase soil
alkalinity thus can be used as soil liming material [6], study shown that boiler ash application to soil may improve plant growth and yield [7,8,9,10]. Many studies conclude that boiler ash application as land application is improving soil quality including nourishing, conditioning and buffering of the soil that will be benifiting to the plant, however as boiler ash may also content some toxic metals especially those from coal combustion contain more heavy metals compared to boiler ash from wood-fired power boiler [11], such as chromium (Cr), cobalt (Co), cuprum (Cu) and cadmium (Cd) that will bioaccumulate in plant tissue, soil and in environment, thus the research on heavy metal reduction in boiler ash is important. Alternative technology to reduce heavy metal content in boiler ash need to be investigated further in order to make boiler ash suitable for land application.

Several studies suggested that the extraction and reduction of heavy metals from boiler ash can be done using absorption through biopolimer [12], using carbon dioxide as its ligand [13] and the removal was conducted by converting the transition metal into complex compounds with organonitrogen or amine compounds [14]. Various factors are determined the formation of complex compounds with heavy metals by two phases (solid-solution) including type and concentration of collectors, particle size and stirring rate, reaction temperature, and contact time of the ligand solution with solid waste tested. In the previous study lauryl amine was used as collector and the results indicated that lauryl amine collector can reduce the heavy metal [15]. In this research a method to reduce the hazard metals has been introduced using stearyl amine in order to explore option for better collector. The objective of this current research is to investigate new amine collector namely stearyl amine as an agent for reducing the heavy metals of boiler ash yielding from pulp and paper industry.

2. Materials and method
These experiments were carried out in the Organic Chemical Laboratory, Faculty of Mathematic and Natural Science, University of Sumatera Utara (USU) Medan and at the Soil Laboratory of PT. Riau Andalan Pulp and Paper (PT. RAPP) Pangkalan Kerinci, Pelalawan, Riau. The samples used were ash obtained from the combustion of boiler ash pulp and paper mill of PT. RAPP. All required chemicals including stearyl amine as collector, ethanol and n-hexane as media were ordered from EMerck.

2.1. Samples preparation
Prior to oven dry at 100°C for 30 minutes, the boiler ash samples were prepared and smoothed by using 400 mesh sizes sieves. Each of 5 g of boiler ash samples was prepared and separated into 9 samples whereas 1 sample for control (check), 4 samples for ethanol treatment and 4 samples for n-hexane treatment respectively.

2.2. Treatment application
Into 2 Erlenmeyer of 250 ml, each was filled with 5 g boiler ash and mixed with 5 g of stearyl amine collector and 30 ml of ethanol solvent. These mixtures were stirred using rotary and shaker for 4 hours and 8 hours respectively. After the stir process completed, the mixture was left for a moment to allow the upper and lower layers are formed and then using a separation funnel the two layers were separated. The first layer in the bottom part as slurry was dried using an oven to obtain dried sample product. After completing the first treatment combination for 5 g stearyl amine and ethanol solvent, this protocol was also implemented for 15 g stearyl amine in ethanol solvent. Follow the same procedures as described above for ethanol solvent, the works were also conducted for n-hexane solvents simultaneously, where mixtures of stearyl amine at 5 g and 15 g are prepared and mixed with 30 ml of n-hexane solvent each. The same procedure is followed until the final product is ready for analysis with ICP.

2.3. Analysis
In order to determine the heavy metal content, these final products of each treatment were prepared and analyzed using ICP.

3. Results and Discussion
Stearyl amine has a long chain as collector that able to absorb the heavy metals. As the final result of the mixing process of the solutions and boiler fly ash, there is a substance that floats on the surface which then turn into solid form of which it has been reduced the heavy metal content of boiler fly ash. These solid was analyzed further using the ICP equipment to evaluate their heavy metal content reduction.

These whole experiment results indicated that the 15 g stearyl amine collector in n-hexane solvent consistently reduces heavy metal content from boiler ash. It is obvious that the 4 hours process time produce more reduction compared to 8 hours for all elements tested (Figure 1, Table 1). The reduction achievement for 4 hours process time of each element is 40%, 43%, 55%, 67% and 76% for B, Cr, Co, Cu and Cd respectively (Table 1). These results showed that the reduction of heavy metal content with stearyl amine collector were far greater compared to results using lauryl amine collector in the previous study [15].

Figure 1. Reduction of heavy metal from boiler ash with 15 g stearyl amine collector in n-hexane solvent

Table 1. Concentration of heavy metals before and after treatment using stearyl amine collector in n-hexane solvent for 4 and 8 hours process time

| Element | Concentration (mg/kg) | Reduction (%) |
|---------|------------------------|---------------|
|         | Before | After 4 hours | After 8 hours | After 4 hours | After 8 hours |
| B       | 223.92 | 134          | 177          | 40.2           | 21.0           |
| Cr      | 13.14  | 7.5          | 10.6         | 42.9           | 19.3           |
| Co      | 5.99   | 2.7          | 3.9          | 54.9           | 34.9           |
| Cu      | 38.9   | 12.8         | 21.2         | 67.1           | 45.5           |
| Cd      | 3.69   | 0.9          | 2.5          | 75.6           | 32.2           |

3.1. Boron (B)
Boron content only reduced when higher dosage at 15 g of stearyl amine was used, while lower dosage at 5 g, stearyl amine collector was not able to reduce boron content, instead boron content was increased in both types of solvent and length of process time (Table 2). Between the solvents, n-hexane treatment reduces boron content better than ethanol solvent. Treatment with n-hexane solvent for 4 hours process time produced the highest reduction of boron content at 40.2% compared to 8
hours process time which only 21%. The efficiency was almost 50% between 4 hours and 8 hours process time.

Boron is essential and micro element for plant; it works in cell fission and protein synthesis. High boron content will harm plant and cause toxic to plant. In the soil boron is formed in borate acid (H₃BO₃) with level of 7-80 ppm. This treatment results able to reduce the boron content for 40.2% to 134 ppm, however these results are still above the required level.

| Dose (gr) | Solvent | Length of Process Time | Reduction to control (%) |
|-----------|---------|------------------------|--------------------------|
|           |         | 4 hours | 8 hours | 4 hours | 8 hours |
| Control   |         | 223.92  |         |         |         |
| 5         | Ethanol | 230     | 226     | -2.7    | -0.9    |
|           | n-Hexane| 259     | 262     | -15.7   | -17.0   |
| 15        | Ethanol | 219     | 192     | 2.2     | 14.3    |
|           | n-Hexane| 134     | 177     | 40.2    | 21.0    |

**3.2. Chromium (Cr)**

Chromium content was also successfully reduced by treatment of stearyl amine collector and ethanol and n-hexane solvents, especially with 15 g stearyl amine (Table 3). The shorter the process time which was 4 hours was better than 8 hours. This is was good result and become an advantage as it needed less process time. As high as 42.9% chromium reduction occurs on the treatment n-hexane solvent at 4 hours process time, this treatment combination produced the highest chromium reduction.

| Dose (gr) | Solvent | Length of Process Time | Reduction to control (%) |
|-----------|---------|------------------------|--------------------------|
|           |         | 4 hours | 8 hours | 4 hours | 8 hours |
| Control   |         | 13.14   |         |         |         |
| 5         | Ethanol | 12.2    | 12.2    | 7.2     | 7.2     |
|           | n-Hexane| 13.5    | 14      | -2.7    | -6.5    |
| 15        | Ethanol | 12.4    | 12.8    | 5.6     | 2.6     |
|           | n-Hexane| 7.5     | 10.6    | 42.9    | 19.3    |

Chromium is an essential element for plant, used by plant in the form of Cr (III) for sugar metabolism. Cr was tied up and absorbed more easily by acid soil. Consider boiler ash for land application will be applied in peat soil area where the acidity of peat soil is higher, it is very important and a must to reduce the Cr content from boiler ash.

**3.3. Cobalt (Co)**

All treatment combinations able to reduce cobalt content and the reduction were ranged from 1.5% – 54.9%. The gap was significant and obvious that the 15 g stearyl amine with n-hexane solvent for 4 hours process time was the best treatment combinations that produce the highest cobalt reduction at 54.9% (Table 4). Within the 15 g stearyl amine treatment, only n-hexane treatment combination showed that the shorter process time is better, where the cobalt reduction is higher.
Table 4. Cobalt content after stearyl amine treatment compared to control

| Dose (gr) | Solvent | Length of Process Time | Reduction to control (%) |
|-----------|---------|------------------------|--------------------------|
|           |         | 4 hours | 8 hours | 4 hours | 8 hours |
| Control   |         | 5.99    |         |          |         |
| 5         | Ethanol | 5.3     | 5.2     | 11.5    | 13.2    |
|           | n-Hexane| 5.8     | 5.9     | 3.2     | 1.5     |
| 15        | Ethanol | 5.2     | 4.4     | 13.2    | 26.5    |
|           | n-Hexane| 2.7     | 3.9     | 54.9    | 34.9    |

3.4. Cuprum (copper)
Cuprum content reduced in all treatments combination of stearyl amine collector and both ethanol and n-hexane solvents (Table 5). The 15 g dosage produced higher reduction in all solvents combination compared to the 5 g stearyl amine dosage. The shorter 4 hours process time produced higher reduction compared to 8 hours. The highest cuprum reduction was 67.1%, and this was as the result of treatment stearyl amine collector at 15 g with n-hexane solvent in 4 hours process time.

Both soil and plant can accumulate cuprum in the environment. Higher cuprum content in the soil reduce plant diversity and reduce microorganism activity. The stearyl amine treatment has a potential to reduce the content of cuprum from boiler ash, where 67.1% reduction was achieved when using n-hexane as solvent in 4 hours process time. This research needs further improvement in order to get the optimum reduction required.

Table 5. Cuprum content after stearyl amine treatment compared to control

| Dose (gr) | Solvent | Length of Process Time | Reduction to control (%) |
|-----------|---------|------------------------|--------------------------|
|           |         | 4 hours | 8 hours | 4 hours | 8 hours |
| Control   |         | 38.9    |         |          |         |
| 5         | Ethanol | 28      | 27.1    | 28.0    | 30.3    |
|           | n-Hexane| 34.7    | 37.2    | 10.8    | 4.4     |
| 15        | Ethanol | 26.1    | 24.4    | 32.9    | 37.3    |
|           | n-Hexane| 12.8    | 21.2    | 67.1    | 45.5    |

3.5. Cadmium
All treatments of stearyl amine collector with both solvents ethanol and n-hexane were able to reduce cadmium content from boiler ash sample (Table 6). In general, process time of 4 hours reduced heavy metal higher than 8 hours. The highest cadmium reduction at 75.6% shown by 15 gram stearyl amine in n-hexane solvent with 4 hours process time.

Accumulation of cadmium content in the water, air and soil often occurred in the industrial area. Cadmium in the soil and water can be absorbed by plant roots, while cadmium in the air can be absorbed by plant leaves, especially those plants that have hairy leaves. Cadmium is a toxic element and the limit threshold is 0.01 ppm. This research showed that the highest reduction of cadmium content from boiler ash resulted from 15 g stearyl amine collector in n-hexane solvent for 4 hours length of process time which was 75.6% reduction or 0.9 ppm. However this result was still above the threshold limit and indicates further research was required.
Table 6. Cadmium content after stearyl amine treatment compared to control

| Dose (gr) | Solvent   | Length of Process Time | Reduction to control (%) |
|-----------|-----------|------------------------|--------------------------|
|           |           | 4 hours | 8 hours | 4 hours | 8 hours |
| Control   |           |         |         |         |         |
| 5         | Ethanol   | 2.4     | 2.3     | 35.0    | 37.7    |
|           | n-Hexane  | 3.1     | 3.2     | 16.0    | 13.3    |
| 15        | Ethanol   | 2.3     | 2.7     | 37.7    | 26.8    |
|           | n-Hexane  | 0.9     | 2.5     | 75.6    | 32.2    |

This research results confirmed that stearyl amine collector in n-hexane solvent can be used to reduce heavy metal content from boiler ash, and also it was better than lauryl amine collector as shown in the previous research by Sembiring MP, et al. 2017, however further research effort was required to continue study and optimize the results in order to ensure that boiler ash can safely be used for land application.

4. Conclusion
Reduction of transition metal content such as B, Cr, Co, Cu and Cd from boiler ash can be done successfully using stearyl amine collector in both ethanol and n-hexane solvent. The 15 g stearyl amine in n-hexane solvent for 4 hours length of process time produced the highest reduction in all tested element consistently and the reduction percentage of each element was 40%, 43%, 55%, 67% and 76% for B, Cr, Co, Cu and Cd respectively. Reduction of heavy metals content from boiler ash using stearyl amine collector is much higher compared to lauryl amine collector as shown in the previous study.

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